QUALITATIVE CHEMICAL ANALYSIS

Certain Principles and Methods used in Identifying Inorganic Substances together with a Systematic Survey of the Chemistry of these materials

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Based Upon The Text By
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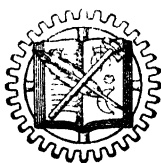
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PREFACE

This attempt to modernize a venerable text in Qualitative Analysis was undertaken with distinct trepidation; the authors realizing the amount of labor involved in a survey of the field of inorganic reactions, as well as the difficulty of interpreting the change now developing in the theory of the subject.

The text by Prescott and Johnson was written during the period when analytical chemistry was a major field in which many of the students expected to labor when finished with their period of training. The special branches of physical chemistry were in their infancy or as yet unborn, and organic chemistry was largely concerned with the synthesis of complex products from simple materials. Industrial development was coming of age, and the importance of analytical control of raw materials and of finished products was generally recognized. It is not surprising, therefore, that time was available in the curriculum for ample laboratory work in chemical analysis. Today the situation is changed. Various aspects of chemistry have been elaborated into new courses until there is keen competition for space in the student's schedule. Furthermore, many of the more obvious problems in chemical analysis have been solved, till the control man in the plant is no longer a research chemist, but a routine worker trained for the particular job.

Under such conditions it is not strange that the point of view from which the course in analytical chemistry is given has changed. It is no longer a course aimed at the development of originality in the student. Rather, it is intended to acquaint him with the methods, the resources, and the limitations of chemical analysis. On that basis, the emphasis is shifting increasingly to a consideration of the theoretical basis of the conditions necessary to obtain satisfactory results.

The remarkable vitality of the older book, which causes it still to find an honored place on the reference shelf of many chemists, is probably due to several causes. First, it covered a wide range of experimental fact. Second, the material was arranged in such a way as to make it unusually accessible for reference. Third, there were copious references to the original literature and to the more extended treatises and dictionaries. From the modern point of view three shortcomings may be listed. (1) the theory of the subject was under emphasized, (2) the references were largely to the earlier literature, much of which is not available in the younger libraries, and (3) the analytical procedures were frequently given in outline form

rather than being described with reasonable fullness. Probably thirty years ago these weaknesses would have been regarded as sources of strength, for at that time analytical chemistry was largely an art to be learned by practice, and the student was expected to try alternative procedures in the laboratory and discover for himself their relative advantages.

In the present book the attempt has been made to retain the excellent features of the older text, and at the same time to expand or to modify certain parts of it in such a way as to make it more useful as a text to accompany the present courses in qualitative analysis. Thus, the range of information and the orderly arrangement of descriptive material under the individual metals and acids are essentially the same as before. The information itself, however, has been carefully scrutinized in the light of more recent literature, and where necessary the statements have been corrected to correspond to present knowledge. At the same time the references have been changed generally to the newer articles, since these are more available and will, themselves, refer to preceding work in the field. In cases where the conflicting statements of the literature were hard to reconcile, the same practice has been followed as before, with references given to both sides of the question.

Part I of the book has been expanded considerably so as to include a more adequate discussion of the theory of qualitative analysis. The assumption has been made that the student is already acquainted with reversible reactions and the theory of ionization from the course in general chemistry. Therefore the treatment of these topics has been undertaken from the point of view of review and extensive application, rather than that of presentation for the first time. In keeping with this assumption, attention is directed frequently to the fact that the simpler generalizations in the theory of analytical chemistry are in the nature of approximations which are useful as a means of establishing some sort of order among a large number of facts, but which may fail to apply in particular cases. Since the major advances in the past have been made by studying the facts which were exceptions to the existing theories, it is hoped that the present treatment, far from discouraging the student in its emphasis on uncertainties, will lead him to a realization that chemistry is still in the process of development, with live problems available everywhere for one who wishes to work in the field.

In rewriting the procedures for laboratory work, it has been recognized that less time is available today than formerly for practice in analysis. Therefore the student will depend less on the results of his own varied experimentation than on the discussions in class and on the notes which accompany the directions. For this reason it seems desirable to set up various well defined boundaries for the laboratory work, including the range of material covered, the concentrations studied, and the general accuracy expected. Detailed directions are given for the analysis of solu-

tions and of dry unknowns, covering twenty-three metals (including ammonium ion) and eleven acid radicals other than the negative ions of the metals. The student is expected to use about fifteen cubic centimeters of solution for analysis, this amount normally containing from twenty to one hundred milligrams of each of the substances to be identified. Within these limits the procedures have been tested and are known to be reliable, the notes accompanying the directions indicating the importance of particular conditions specified. In handling quantities considerably different from the above, distinct modifications of procedure are frequently necessary; therefore the student should receive definite warning if he is expected to deal with a more extended range of concentrations. In such a case reasonable time must be spent discussing the changed technique involved.

The laboratory method is undoubtedly the most interesting way of acquiring chemical knowledge, but it is essentially time consuming. With the subject constantly expanding, it is impossible for the student to verify any wide range of experimental fact for himself. Therefore it is becoming general practice to cover in the laboratory only such typical situations as will serve to illustrate the material of the course. In addition to this the student is expected to become acquainted with a fair amount of supplementary information as supplied by the text. And as he browses through the book the authors hope that he may develop a confidence in it that will cause it to become a prized member of his own budding library.

In gratefully acknowledging our indebtedness to the vast army of workers and diligent compilers in the field of chemistry, we assume responsibility for the errors that occur, and trust that those who use the book may feel sufficiently friendly toward it to inform us of any mistakes they discover.

R. K. M.
B. A. S.

Ann Arbor, Michigan,
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PART III. — THE NON-METALS

BIBLIOGRAPHY

The object of a scientific bibliography should be primarily to inform the reader concerning sources of data quoted and secondarily an acknowledgment of indebtedness to the workers who have gleaned the evidence. With such a purpose in mind the authors of this compilation have made a special effort to insure the accuracy of all references, first by checking each one themselves and then by having an assistant verify every one in the final copy of the manuscript. This was accomplished through direct consultation of the article cited or, when not available, by comparing the data in two abstract journals. Through this system it is hoped that errors have been reduced to a minimum.

Concerning the secondary intent the writers have been, perhaps, a little less fortunate. In general, when a statement has been encountered in several books without citation, i.e., has apparently become common property, no reference is given here. An exception to this policy has been made, however, in certain cases where the work of an early investigator is deemed of historical interest. Furthermore, when many workers have published articles on the same subject no attempt has been made to give a complete list of references. One or two papers have been mentioned with the belief that a satisfactory introduction to the literature might thus be afforded. Of course the dangers here are that full credit may not be given where due and that an article of lesser value may be mentioned while one of greater importance is omitted. It is hoped that the reader will co-operate by informing the authors of such unintentional mistakes.

Article *references* and *abbreviations* have been given according to the style advocated by *Chemical Abstracts* as published in the November 20, 1931 issue. There is one exception to this rule, i.e., the abbreviation *Chem.* or *Chim.* has been decreased to *Ch.*

Often reference to an article and to the C.A. abstract have both been given. This is for the benefit of those who may not have access to the journal cited or may be unfamiliar with the language in which it is printed. Occasionally a reference only to Chemical Abstracts has been given (in parentheses) because the journal of original publication is known to be less widely available.

The " monumental " handbooks, encyclopedias, etc., that the authors have found useful — in many cases of inestimable value — during the

assembly of data for this book and to which references have been repeatedly given are listed below.

Abbreviations Used in Text	Title in Full, Publisher and Date of Publication
Abegg	Handbuch der Anorganischen Chemie, S. Hirzel, Leipzig, 1905–.
A. S. T. M.	American Society for Testing Materials, Philadelphia.
Beckurts	Die Methoden der Massanalyse, Friedr. Vieweg und Sohn, Braunschweig, 2nd ed., **1931**.
Beilstein	Beilsteins Handbuch der Organischen Chemie, Julius Springer, Berlin, 4th ed. 1918–.
Caven and Lander	Systematic Inorganic Chemistry, D. Van Nostrand Co., Inc., New York, **1930**.
Ephraim	Anorganische Chemie, Theodor Steinkopff, Dresden, 4th ed., **1929**.
Evans	Metals and Metallic Compounds, E. Arnold & Co., London, **1923**.
Fehling	Neues Handwörterbuch der Chemie, Friedr. Vieweg und Sohn, Braunschweig, **1871-1930**.
Friend	Textbook of Inorganic Chemistry, Charles Griffin & Company, London, 1914–.
Gmelin	Gmelins Handbuch der anorganischen Chemie, Verlag Chemie, Leipzig-Berlin, 8th ed., 1926–.
Gmelin-Kraut	Handbuch der anorganischen Chemie, Carl Winter, Heidelberg, 7th ed.
Hillebrand and Lundell	Applied Inorganic Analysis, J. Wiley & Sons, Inc., New York, **1929**.
Hopkins	Chemistry of the Rarer Elements, D. C. Heath and Co., New York, **1923**.
I. C. T.	International Critical Tables, McGraw-Hill Book Company, Inc., New York, **1926-31**.
Latimer and Hildebrand	Reference Book of Inorganic Chemistry, The Macmillan Company, New York, **1929**.
Margosches	Die Chemische Analyse, Ferdinand Enke, Stuttgart. (A series of monographs.)
Mellor	Comprehensive Treatise on Inorganic and Theoretical Chemistry, Longmans, Green and Co., New York, 1922–.
Mitchell	Recent Advances in Analytical Chemistry, P. Blakiston's Son & Co., Inc., Philadelphia, **1931**. Vol. II.
Muspratt	Muspratt's Theoretische, praktische und analytische Chemie. Friedr. Vieweg und Sohn, Braunschweig, 4th ed. + suppl., 1888–.
Noyes and Bray	System of Qualitative Analysis for the Rare Elements, The Macmillan Company, New York, **1927**.
Rüdisüle	Nachweis, Bestimmung und Trennung der chemischen Elemente, M. Drechsel, Bern, 1913–.
Stieglitz	Elements of Qualitative Chemical Analysis, The Century Co., New York, **1917**.
Thorpe	Dictionary of Applied Chemistry, Longmans, Green and Co., New York, **1921-7**.
Ullmann	Enzyklopädie der technischen Chemie, Urban & Schwarzenberg, Berlin, 2nd ed., 1928–.

PART I

THE PRINCIPLES OF ANALYTICAL CHEMISTRY

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THE AIM OF QUALITATIVE ANALYSIS

§1. **Qualitative Analysis,** as commonly studied, bridges the gap between general chemistry and quantitative analysis. It deals chiefly with the chemistry of aqueous solutions of inorganic substances. The ground covered is distinctly more limited than that of the usual college course in general chemistry. Some twenty, only, of the common metals are usually included and ten or a dozen of the simpler acids. The problem faced is that of recognizing the presence of each of these in the presence of various combinations of the others.

It would simplify the situation very much if there were only available a corresponding number of specific reagents, one for each substance to be identified, giving unmistakable tests and giving positive results with very minute amounts. In that case it would only be necessary to place separate portions of the unknown in a series of test tubes, add the reagents and note the results. If it could be done that way the course in qualitative analysis could be given in much shorter time than is now required, in fact it could very well be given as an adjunct of general chemistry involving a few weeks of laboratory practice and a few nights of committing formulas to memory.

It so happens, however, that there are relatively few specific tests available, so the chemist is immediately plunged into a series of preliminary separations before the final tests can be applied. The separations involve a considerable fund of information about similarities and differences of behavior of the various metals and acids with each other. But for one who has this information in useful form a surprisingly varied series of separations becomes possible. To illustrate this it is only necessary to recall the behavior of nitrates of silver, lead and iron with such reagents as hydrochloric acid, potassium iodide, sulfuric acid, hydrogen sulfide, sodium hydroxide and ammonium hydroxide. These reactions are tabulated in Table 1.

On the basis of these reactions silver and lead might be separated from each other by four different methods.

(1) HCl in dilute solution would precipitate silver as the chloride, leaving lead in solution.

(2) H_2SO_4 in dilute solution would precipitate lead as the sulfate, leaving silver in solution.
(3) NaOH, used in excess, would precipitate silver as the oxide, redissolving the lead hydroxide first formed to give a solution of sodium plumbite.
(4) NH_4OH, used in excess, would precipitate lead as the hydroxide, redissolving the silver oxide first formed to give a solution of silver ammonia nitrate.

In the same way, lead and iron or silver and iron might be separated from each other by five different methods (the separation somewhat incomplete when precipitating lead as the chloride from concentrated solution, or when precipitating silver as the sulfate from concentrated solution).

TABLE 1

SOME REACTIONS* OF SILVER, LEAD AND FERRIC IONS

	HCl	KI	H_2SO_4	H_2S	NaOH	NH_4OH
$AgNO_3$	AgCl	AgI	Ag_2SO_4	Ag_2S	Ag_2O	Ag_2O $Ag(NH_3)_2NO_3$
$Pb(NO_3)_2$	$PbCl_2$	PbI_2	$PbSO_4$	PbS	$Pb(OH)_2$ Na_2PbO_2	$Pb(OH)_2$
$Fe(NO_3)_3$	———	$Fe(NO_3)_2$	———	$Fe(NO_3)_2$	$Fe(OH)_3$	$Fe(OH)_3$

* In the squares under each reagent, the upper half is used to indicate the *ordinary* reaction of the reagent; if with larger amounts of reagent a secondary reaction takes place this is indicated in the lower half of the square. A straight line drawn underneath a formula means that this compound precipitates, a line with up-turned ends (└───┘) means that the compound is in solution. If both lines are used the compound is slightly soluble, forming a precipitate from somewhat concentrated solutions of the metal, but not from more dilute solutions.

It might appear from this that the procedure in qualitative analysis should be to provide one's self with a complete chart showing the reactions of the metals and the acids with the common reagents, and then start in running each metal or acid down by using a series of reagents in such order as to separate it from all the others and then add a final test reagent that produces some striking effect to find out if the substance sought is present.

In attempting to devise such a series of operations for each of the metals, it quickly becomes evident that a single reagent is being used in several different series to separate certain metals from the rest. It would be an

obvious saving of time and reagents to carry out this one operation for all the metals at the same time on one portion of the solution. With that in mind the suggestion arises, may it not be possible to select reagents and use them in such an order as to separate the whole list of metals into a number of groups, filtering out each group as it is precipitated and in that way separating all of the metals of the given group from the rest? The metals of the third group to be precipitated will be separated from those of Groups I and II by the reagents used to precipitate the first two groups, and will be separated from the metals of Groups IV, V, etc., by the reagents used to precipitate Group III. The problem would be divided in that way into several smaller problems of dealing with only a few metals at a time. This procedure is the basis for the present systems of qualitative analysis.

It is evident that by varying the choice of group reagents and the order in which they are used many systems might be devised. In judging the value of these various systems, two practical questions are raised. (1) Are they **equally accurate?** (2) Are they **equally convenient?** Of two systems, that one is better which is more accurate and easier to carry out than the other. It frequently happens, however, that one system is more accurate than the other but the second is easier to carry out. In such a case the decision as to which is better depends on which of the two qualities is considered the more important, accuracy or convenience. Without attempting to decide between these two desirable qualities at present, it is obvious that no scheme will be adopted which is seriously lacking in either until an attempt has been made to find another that is less open to criticism. In the end, however, it may prove that no one system can be devised that is best in both respects. As a matter of fact that has actually turned out to be the case.

One is limited in actual analysis to the use of actual reactions. There are of course, a host of these, while the ordinary scheme of analysis employs relatively few of them. But it is only fair to assume that most of them were studied for their availability for qualitative analysis during the latter half of the 19th century when so much of the exploratory work on reactions was being done and when the main field in chemistry was chemical analysis. There may be better separations than the ones now used tucked away in the chemical behavior of the metals with known reagents, but it would be an enormous undertaking to conduct the systematic survey of the field that would be necessary to discover them and prove that they are better. There were many men in the past generations ranking high in chemical achievement who devoted a considerable part of their lives to this problem; there are men now living, but advanced in years (Böttger, Stieglitz, Noyes), who have carried on where these left off. It would take a courageous optimist to attempt a revision of the present system in the belief that it would be easy to improve.

§2. **New reagents** are discovered from time to time and found on study to be useful in analytical chemistry. Thus, in more recent years there have been made available a number of organic reagents that are distinctly better than those formerly used. Probably the greatest hope for improved methods lies in the discovery of more of these specific reagents. Thus far, however, there have been no ways discovered by which one can judge whether or not a given reagent will be of value and so the search for new reagents of this type is essentially empirical and enormously time consuming. Thus far only one man (Feigl) has undertaken a serious search for such reagents.

§3. **Another recent development** in the field of chemistry that has distinct importance for the analytical chemist is the growth of *colloid chemistry* into a separate branch. The colloid chemist is concerned with the physical and chemical behavior of very small particles, particles many times the size of molecules, but much smaller than the individual units of a filterable precipitate. The analytical chemist is continually carrying materials through this stage in converting precipitates into molecules and ions in the dissolving process and in converting ions and molecules into filterable precipitates. In the preparation of colloidal particles the colloid chemist starts with the same materials as the analytical chemist, but tries to stop the process when it has reached the colloidal stage so as to study the properties of the particles in this condition. Thus he has been interested in methods of preparing colloidal solutions, but once these have been prepared he has been concerned with the reverse process of converting colloidal solutions into true solutions or filterable precipitates. In this study he has learned many things that are of immense interest to the analytical chemist. Unfortunately this material is still largely in the nature of specific information about individual cases. Few valid generalizations have thus far been developed that can be taken over directly into the analytical field, but the outlook for the future is promising. Even now the facts of colloid chemistry offer an explanation for many irregularities of analysis that in the past have merely been accepted as experimental fact. In some cases these difficulties have been overcome by applications of the methods of colloid chemistry, and in other cases new errors may be discovered that have not been suspected. On the whole there is reason to hope for distinct improvement of present methods as new experimental work is undertaken from this point of view.

§4. **The present scheme** of qualitative analysis has been developed along the lines above indicated. The question may well be asked, is it satisfactory? The answer is, No! In the present scheme it has frequently been necessary to strike a compromise between accuracy and simplicity. In order that a fair range of ground may be covered in a single semester

it is necessary that the scheme of analysis be fairly simple. On that basis many accurate separations are not used because they are too complex, too tedious and time consuming; and some separations of moderate inaccuracy are used because they are easy and rapid to execute.

It is precisely in the nature of this compromise that qualitative analysis occupies an intermediate position between general chemistry and quantitative analysis. In general chemistry a wide field is covered in relatively short time. It is necessarily impressionistic in character. Generalizations are taught that have only approximate validity. Many of the minor irregularities are smoothed. "Crooked ways are made straight and the rough places plane." This is as it should be, for in the introductory course a large field is being surveyed and it is necessary to set up landmarks that will enable the student to find his way about, see general relations, and form a correct small scale picture of the whole situation. In such a case the material is clearly to be presented only in its simpler aspects, else the student will lose his perspective in a mass of details. It is evident that under such conditions things must be kept simple. If a situation becomes complex it is by that very fact eliminated from the introductory course, except in so far as an occasional side remark may hint of such things in order that the student may be made to realize that what he is getting is essentially an outline into which an enormous amount of detail must be fitted before it discloses the character of every day experience.

In quantitative analysis, on the other hand, one deals with specific situations. A certain substance is to be analyzed, to find out how much of a given constituent it contains. The figures are to be reported to a certain decimal place and to be accurate to within a very narrow range. Under such conditions the essential requirement is that the process used shall give accurate results, that if a given metal is to be separated from others by precipitation, it must be known what volume of solution to use, what conditions to establish in the solution, how much reagent to add and how to add it, and how long to wait for the reaction to take place, in order that the metal may be precipitated within the desired limits of completeness and that the precipitate may be correspondingly pure and definite in composition. Above all, a method must be accurate. If it is inaccurate it is discarded no matter how simple it may be, and if it is the only method that will give results of a desired degree of accuracy, it is the one that will be used regardless of how complex it is. In chemical analysis, experience has taught the fact, and theory later confirmed, that accurate separations are typically slow processes. In general chemistry the student has learned to add a bit of reagent to a solution in a test tube, put his thumb over the end, shake once or twice, and then filter out the precipitate, all in the course of a minute or two. He feels there is something wrong if at any time he is directed to let the precipitate stand as long as five minutes before filtering. And yet in quantitative analysis it is the exceptional

precipitate which can be filtered out after as short a time as half an hour. Frequently one or two hours are allowed, and occasionally in specific cases it may even be recommended that the solution be permitted to stand over night for precipitation. Under such conditions a relatively small amount of ground can be covered in a laboratory period and the material for a semester's work will appear very scanty when presented in outline form.

In qualitative analysis, the traditional content of the course is intermediate between that of general chemistry and quantitative analysis. It is therefore to be expected that the emphasis on those two qualities of simplicity and accuracy will be shifted to a similar degree. The material is part of that covered in the introductory course. But now it may be considered in greater detail, more specific information may be demanded, and a better appreciation had of the conditions under which chemical processes are carried out. Procedures may now be used that were out of place earlier. But since there is still considerable ground to cover in a limited time there are limits set by practical expediency to the time that can be devoted to a single operation.

It is desirable that there should be this natural progression among these courses, for each one is thus a preparation for the one to come and a development from the preceding one. It would be equally desirable to have specific courses in these respective branches developed in accordance with these shifting aims.

It has been indicated that qualitative analysis is an imperfect tool for applied chemistry. The question may well be asked, why study it? The answer is, because it is a logical introduction to chemical analysis which is of fundamental importance in every phase of pure and applied chemistry. In new syntheses in organic chemistry chemical analysis is used to check the results obtained. In industry, chemical control of a process involves chemical analysis of the materials used and of the product formed. Everyone using chemistry to a significant extent should have a reasonable understanding of what chemical analysis can do and what it cannot do. The obvious way to acquire this is by the study of chemical analysis itself.

REQUIREMENTS OF GROUP REAGENTS

§5. In turning to a more direct consideration of the procedures of qualitative analysis it may be worth while to mention some of the qualifications of a satisfactory group reagent in order that the advantages and the disadvantages of those used in the accepted scheme may be better

understood. There are three of these that apply to an important degree in the critical comparison of available reagents. (1) The reagent should *precipitate the metals* of the given group *completely* enough so that the amount that remains in solution can be disregarded. (2) The reagent should form precipitates that are *easy to work with* in carrying out the further steps of separation and identification within the group. (3) The reagent should form precipitates that are reasonably *free from contamination* with later group metals.

§6. **It is important to precipitate the metals of a given group with reasonable completeness,** both in order that the smaller amounts of them may be identified, and in order that they may not interfere by precipitating in later groups and be mistaken for other metals. It is easy to judge the completeness with which a metal will precipitate with a particular reagent at a definite temperature by referring to the solubility of the corresponding compound. This information is available in most of the books on general or analytical chemistry, in such hand books as Van Nostrand's " Chemical Annual," or the " Handbook of Chemistry and Physics," and in such more extended treatments as the dictionaries of solubility by Seidell or by Comey and Hahn. In examining such data one may find several different sets of figures for a given compound, but, while this raises some interesting questions in chemistry, a comparison of these different figures will show that there is no serious problem of determining the approximate completeness of precipitation to be expected. For example, silver chloride is given as having a solubility at 20° of 0.0015 grams per liter. On this basis, if precipitation were carried out in a volume of 100 cc. there would be left in solution 0.00015 g. of silver chloride. As a matter of fact it is well known that the solubility of many precipitates becomes less if excess of the precipitating agent is added. This is true in the case of silver chloride, so the above figure may be considered as a maximum amount to be left in solution.

In order to judge the actual significance of these figures it is necessary to have some notion of the quantities ordinarily handled in analytical chemistry. The funnels and filter papers commonly used in chemical analysis will hold satisfactorily approximately 0.2–0.3 g. of metal in the form of the ordinary precipitate. Of course precipitates vary considerably in their bulk, or relation of volume to weight, so that in the case of a bulky precipitate the above figure is high, while in the case of a dense, compact precipitate it might be possible to handle several times as large a weight. (As instances in point it would be instructive to prepare two solutions, one containing 0.2 g. of iron, as a ferric salt, the other 0.2 g. of lead, and precipitate the two metals as ferric hydroxide and lead sulfate, respectively. Even in the beakers, as the precipitates settle, it will be evident that the two precipitates have different volumes, and, on filtering, this difference

will be still more evident.) With the figure 0.2–0.3 g. considered as a practical upper limit of quantity to be handled, it is necessary next to consider how small an amount of material can be worked with. The usual analytical balance is sensitive to about 0.0001 g. (0.1 milligram). With small errors in the adjustment of analytical weights and in the conditions and methods of weighing, the average single analytical weighing has a practical accuracy of about 0.0005 g. Since it is desirable to keep individual errors well below the lower limit of quantity that can be worked with in order that the cumulative effect of several errors may not exceed this quantity, the solubility of the precipitate being formed should be less than 0.0005 g. in the total volume of solution and of wash water used.

On the basis of these figures, the precipitation of silver as the chloride would be considered a satisfactory procedure so far as this first factor (completeness of precipitation) is concerned. If the total volume of solution and wash water is kept within 100 cc., the amount of silver chloride left in solution (0.00015 g., of which only 75% is silver) would fall within the limit of quantity that could be handled on the analytical balance, and so might be considered as negligible in the determination of silver. Further, this amount is so small that even if it were all precipitated in some later group and carried through the group analysis to the point of appearing when the confirmatory test for one of the other metals is being applied, it would not interfere to a significant extent with the detection of the other metal. As a matter of fact instead of all of it appearing at any one place it would usually be distributed among several precipitates and thus be so reduced in quantity as not to interfere at all with later determinations.

In passing, it might be worth while to touch on the question of accuracy just a bit further. The accuracy of a determination is measured by the ratio of the minimum amount that can be handled to the amount actually being handled. The smaller the ratio the more accurate the process. If one is dealing with 0.2 g. of silver and working with it to a lower limit of 0.0002 g. the accuracy of the process is the ratio 0.0002 : 0.2 or 1 part in 1000. Expressed in another way, the accuracy is 0.1%. Usually the accuracy is stated in terms of the total weight of sample being analyzed, so that if the material is an alloy of which only 40% is silver and a 0.5 g. sample is being analyzed, the accuracy would be considered as 0.0002 : 0.5, instead of 0.0002 : 0.2. The determinations in analytical chemistry are commonly reported to the second decimal place in per cent, and an accuracy of 0.1% is considered satisfactory. There are cases, however, in which constituents present in much smaller quantities than this must be determined. In steel, for instance, it is necessary to keep the content of sulfur below 0.05%. The accuracy of a determination may be increased to satisfy the requirements in such a case either by increasing the size of sample used or by improving the manipulation so that a smaller quantity of material may be effectively handled. Thus, with the above figures, if

the size sample is increased from 0.5 g. to 5 g. the accuracy would be increased tenfold. Or, working with a 0.5 g. sample, if the lower limit of material to be handled could be reduced from 0.0002 g. to 0.00002 g., this would also increase the accuracy of the process tenfold. In actual practice both of these methods are employed.

§7. **The second important requirement** for a satisfactory group reagent is that it should form precipitates that are easy to work with in carrying out the further steps of separation and identification within the group. On consulting a table of solubilities it is found that silver iodide is much less soluble than silver chloride, the figures being, for AgCl, 0.0015 g. per liter, and for AgI, 0.000003 g. per liter. Silver chloride is five hundred times as soluble as silver iodide. On that basis it would appear that it would be even better to precipitate silver as the iodide than as the chloride. But when one considers the readiness of separating silver from the other metals that would precipitate as chlorides and then identifying it, as compared with the difficulty with which one could do that in the case of iodides, it is evident that there is a strong argument in favor of the former. Silver chloride is readily soluble in ammonium hydroxide from which it can be reprecipitated by adding excess of nitric acid. In the case of silver iodide, however, it is necessary to carry out some operation that separates the silver completely from the iodine before satisfactory confirmatory tests can be made. Not only are such separations cumbersome in themselves, but they affect the other metals that might be present in such a way as to make their identification less direct. The slight advantage gained in precipitating silver in a less soluble form would be more than offset by the difficulties encountered in further examination of the precipitate. Silver chloride is sufficiently insoluble that, ordinarily, one need not worry about the amount that remains in solution. It would be splendid if all the other precipitates in qualitative analysis were as satisfactory in this respect as silver chloride.

In addition to difficulties occasionally encountered because of extreme insolubility, a reagent may be unsatisfactory because of the physical character of the precipitate formed. The ideal precipitate is sufficiently coarse grained so that it will be retained readily by a loose textured filter paper, will not clog the filter paper, can be washed readily, and can be transferred easily from the filter paper to a beaker or test tube. As typical precipitates to study these qualities one might compare barium sulfate, ferric hydroxide and silver chloride. (Prepare the precipitates under similar conditions, using 0.05–0.1 g. of metal in 25–50 cc. of solution, adding the reagent in slight excess, shaking or stirring a short time and finally filtering.) Barium sulfate is so finely divided that some of it runs through the ordinary filter paper used in qualitative analysis. Ferric hydroxide is gelatinous and clogs the pores of the paper making the process

of filtering rather slow, besides clinging so that it is difficult to rinse off the paper. Silver chloride coagulates into a curdy precipitate which filters out well, does not clog the filter, and is easily separated from the paper later.

It is possible to modify the physical character of many precipitates by controlling the conditions under which they form, and in that way make them much more satisfactory for analytical manipulation. Thus, barium sulfate may be distinctly improved by precipitating at a higher temperature and letting the solution stand for half an hour or longer before filtering. In the same way ferric hydroxide may be improved by precipitating from a hot solution in the presence of a large amount of ammonium chloride with slight excess of ammonium hydroxide, and boiling the solution several minutes. But, in some cases, the precipitates are not so easily obtained in satisfactory form. Some of the sulfides, such as zinc, manganese and iron, commonly come down as semi-colloidal precipitates that run through the filter paper with surprising readiness. Others, such as silver sulfide and nickel sulfide may be obtained in good condition if sufficient care is taken in regulating the amount of reagent used, but with excess of hydrogen sulfide colloidal precipitates are obtained. It is evident that if one had a choice in the matter he would avoid the use of such compounds in his ideal scheme of analysis.

§8. **The third important requirement** for a satisfactory group reagent is that it should form precipitates that are reasonably free from contamination with later group metals. This requirement is essentially the reverse of the first one. Both are concerned with a satisfactory separation of the given group from later groups. In the first requirement this involved the completeness of precipitation of the given group so that small amounts of metals belonging in the group could be identified and so that not enough would escape precipitation to interfere with tests in any of the later groups. In the present case there is the problem of preventing the carrying down in one group of sufficient quantities of any of the later group metals to cause false indications in the given group or to affect seriously the identification of such metals in their proper places. This is a problem of more serious dimensions than is commonly realized.

Just as there are no substances which can be considered as absolutely insoluble, so there are few substances that are absolutely soluble; that is, so soluble that a limited amount of solvent will dissolve an indefinitely large amount of solute. There are only degrees of solubility. This is sometimes indicated by the use of qualifying terms such as, very slightly soluble (insoluble), slightly soluble, moderately soluble, readily soluble and very soluble (see Table 32). The separation of one group of metals from later groups is based on the lower solubility of a certain salt of these metals than of the same salt of later group metals. But the solubility table may

show that there is only a moderate difference in this respect. In such a case it is difficult to precipitate the earlier group completely when large amounts of the later groups are present without some precipitation of these metals at the same time. In fact the relative solubility imposes a definite limit as to the completeness of such a separation. Thus, lead is commonly precipitated in a certain group by hydrogen sulfide in slightly acid solution, while zinc is precipitated in a later group by hydrogen sulfide in slightly alkaline solution. Both lead and zinc sulfides are so slightly soluble that they are commonly classed with that large group of substances that are called insoluble. Both of them are much less soluble than silver chloride. The solubility figures commonly referred to in this connection indicate that zinc sulfide is approximately seventy times as soluble as lead sulfide. On that basis one would expect that the separation in the above case would only lower the concentration of the lead to one-seventieth that of the zinc. If this does not precipitate the lead completely enough for the purpose in hand it may be necessary to include some zinc sulfide in the earlier group.

A more insidious source of unsatisfactory separations lies in a peculiar effect known as *adsorption*. Many precipitates, in forming, carry down other substances that are readily soluble. This effect is treated at some length in colloid chemistry. It appears to be quite specific in nature both as to the precipitate that does the adsorbing and as to the substance adsorbed. Many instances of it are known, but few generalizations have been developed that make it possible to predict when it will occur. For that reason it has been overlooked frequently until more careful quantitative studies had shown that it was the real source of certain irregularities. According to the colloid chemist it probably occurs in the great majority of precipitation reactions and the best the analytical chemist can hope for is that it will occur to a slight enough extent in particular cases to be considered a negligible source of error. Sometimes it manifests itself by preventing the precipitate from coagulating in the usual way, as in the case of precipitation of silver chloride in a solution containing chromic ion. Instead of the usual curdy precipitate a colloidal suspension is obtained that has struck despair to the hearts of many unsuspecting students. More commonly it results merely in precipitating smaller quantities of a later group metal in an earlier group, as in the precipitation of small amounts of zinc with copper sulfide or of nickel with chromic hydroxide. Occasionally it may even result in relatively complete removal of a metal from a later group, as in the carrying down of zinc by aluminum hydroxide.

In addition to avoiding adsorption while precipitating one group of metals, the reagent should not permit secondary reactions to occur by which later group metals are also precipitated. It is possible to precipitate aluminum hydroxide with excess of ammonium chloride present and using small excess of ammonium hydroxide, under such conditions that

manganous hydroxide will not precipitate. But in an alkaline solution manganese is very easily oxidized to manganic hydroxide by atmospheric oxygen, and this compound is sufficiently insoluble so that it does not stay in solution. Again, moist hydrogen sulfide undergoes oxidation very readily; readily enough so that if barium happens to be in the solution when precipitating the sulfides of other metals, small quantities of the barium may be lost as the sulfate.

A further difficulty in group separations may occur if the available reagent is not, within reasonable limits, the pure reagent it is supposed to be. Obvious impurities such as those derived from inadequate purification in manufacture are not included in the discussion at this time, though the alert chemist will realize that it may be necessary to test this matter by direct experiment. But a reagent which is of sufficient purity in its original container may not remain so in the usual storage in reagent bottles. Thus ammonium hydroxide regularly absorbs sufficient carbon dioxide from the air to give an appreciable precipitate with barium chloride, so it is not surprising if the ammonium hydroxide used to precipitate certain of the metals as hydroxides should at the same time precipitate certain of the other metals as carbonates. A solution of sodium hydroxide attacks its glass container sufficiently to cause slow formation of a sediment of silicates in the bottle as well as a dilute solution of sodium silicate in the reagent. The latter is frequently the source of a slight gelatinous precipitate much resembling aluminum hydroxide in appearance. A solution of ammonium sulfide is so readily oxidized that a few minutes' exposure to the air changes the solution from colorless to yellow. The oxidation does not stop with formation of poly-sulfide, $(NH_4)_2S_x$, in which x may have a value as high as 5; but may even be carried as far as to thiosulfate, $(NH_4)_2S_2O_3$. Under such conditions it is evident that separations based on the use of ammonium sulfide may be seriously complicated by the presence of various other sulfur containing anions, and in the case of an old reagent there is the further possibility that it no longer contains any sulfide ion.

The obvious qualifications to be looked for in a satisfactory group reagent have not been exhausted in discussing the three important ones listed above. Others might be mentioned hardly less significant than those discussed and sometimes having more weight in turning the scales against particular reagents than any of the above. For instance, a reagent should not interfere with later separations, or, if it does interfere, should be easily removed. Thus, certain of the phosphates are sufficiently insoluble to be precipitated in very dilute acid solution as a fair separation from certain other metals. But the other metals are commonly separated later in alkaline solution and, in attempting to make the solution alkaline for such separation, the phosphates would precipitate. This would not be objectionable if it were easy to remove the phosphate ion as an intermediate

step, but such removal is an involved analytical procedure to be avoided if possible. A reagent should be stable,[1] readily available,[2] inexpensive,[3] harmless[4] and easy to use.[5]

Finally, a reagent used for the separation of a group should precipitate a reasonable number of metals. If it precipitates too few, little has been accomplished toward simplifying the procedure. If it precipitates too many, the separations within the group become too complex, involving practically a redissolving and further division into groups which are then called sub-groups. The ideal arrangement for twenty metals would be a series of reagents that would divide the twenty into five groups of four metals each. Other things being equal there would be fewer steps involved in systematic testing for the twenty metals on that basis.

§9. **A more detailed consideration of the actual scheme of analysis** to be followed in this book may now be considered. There are several general schemes in common use, differing from each other in relatively minor ways. There is no one scheme that meets universal approval; there is no scheme that is even reasonably satisfactory when judged on the basis of the requirements for group reagents listed above, though none of those requirements is of itself unreasonable. The truth of the matter is that in setting out on the task of identifying some twenty individual metals in a possible mixture, there is available only a relatively crude, cumbersome, and even frail set of machinery with which to do the work. But this is so typical of the general situation in attacking chemical problems that a course in Qualitative Analysis properly conducted should give the student an honest recognition of this and an appreciation of chemical methods and chemical points of view.

In the present scheme the twenty-three metals (counting ammonium ion as a metal) are divided into six groups by the successive use of reagents as shown in the following table.

[1] Ammonium hydroxide and chlorine water both lose strength on standing.

[2] Many of the organic reagents proposed are ruled out because they are not commercially available.

[3] Chloroplatinic acid is an extreme case of a reagent long used in the separation of potassium from sodium, that persisted in spite of its cost until a distinctly cheaper substance was found that would work as well.

[4] Sodium or potassium cyanide is the classic poison about which the student receives due warning. As a matter of fact hydrogen sulfide is probably more of a menace than potassium cyanide.

[5] There are now available many of the common gases in compressed or liquid form in steel cylinders. These are excellent in many ways, but there is a mechanical difficulty in providing a smooth, readily adjustable flow of gas from them, which is a decided source of inconvenience.

TABLE 2

DIVISION OF METALS INTO GROUPS

Reagent	Group	Metals
HCl	I	Ag, Hg, Pb
H_2S (soln. acid)	II	Hg, Pb, Bi, Cu, Cd, As, Sb, Sn
NH_4OH(NH_4Cl present)	III	Fe, Cr, Al
H_2S (soln. alkaline)	IV	Co, Ni, Zn, Mn
$(NH_4)_2CO_3$	V	Ba, Sr, Ca
No group reagent	VI	Mg, Na, K, NH_4^+

A mere glance at this outline shows that the scheme is not an ideal one. Mercury and lead are found in both Groups I and II. This necessitates looking for these metals in two different places, besides involving separation of the metal from the others in Group II even though it has been identified in Group I. Group II includes eight metals, so many that the process of analysis of this group is distinctly complex. This is recognized in the development of some courses by omitting the last three metals in the list (the arsenic division of Group II) in the first general consideration of Group II in relation to the other groups. After the six groups have been studied the arsenic division is then added and the various complications which it makes discussed; including problems of precipitation of the group, additional difficulties of analysis of Group II, and irregularities in other groups that may arise from inaccurate group separations. Groups III and V are fair in number of metals included, but Group IV is the best in this respect. This does not mean that Group IV is the easiest one to analyze. As a matter of fact there are other complications which more than offset this one factor and make Group IV rather less satisfactory than some of the others. Other difficulties in the use of these reagents have been indicated in the examples given to show the shortcomings of some of the chemicals that might be used in working out a general system of group separations.

Enough has been said to make it clear that the procedure in qualitative analysis is not a mere dumping in of some indefinite excess of reagent, followed immediately by filtering, washing, and examining the precipitate thus obtained. A host of special precautions are necessary if the separation is to be even approximately as successful as it can be made. It might be possible to write out these details with extreme fullness so that the student could carry out the work in the laboratory in purely mechanical fashion, but this would make the course entirely a training in manipulation and in rote memory. It would be applicable only within a certain limited range of concentrations of materials and would not give practice in the intelligent modification of procedures to fit special conditions. In order that the student may have an intelligent grasp of the methods of qualitative

analysis it is necessary that he have a good understanding of certain phases of the theory of chemical reactions, especially in aqueous solutions. For that reason a review and an extension of some of these topics is now presented. Following that the discussion will be continued. (See §23.)

THE THEORY OF REVERSIBLE REACTIONS

§10. **The Law of Mass Action.** — The most important practical generalization in chemistry is the law of mass action. This is concerned with the fact that the rate at which a reaction takes place depends in part upon the concentrations of the reagents. In this statement are involved two ideas that require some further discussion: (1) rate of reaction, (2) concentration of reagent.

The concept of rate involves the two ideas change and time. It may be expressed in units showing the amount of change taking place in unit time or the length of time required for unit change to take place. Thus, the rate at which an automobile is travelling may be expressed as 40 miles per hour; the rate at which a wheel is turning, as 1500 revolutions per minute; the rate at which the earth is revolving, as once in 24 hours; and it takes approximately 28 days for the moon to cover its orbit about the earth. In chemical reactions the change taking place is the consumption of reagents and the formation of products. If it is easier, experimentally, to measure the concentration of one of the substances than that of any of the others, whether reagent or product, then the rate of the reaction may be measured by determining either how long it takes for unit change of concentration of this substance to take place, or how much change of concentration takes place in unit time. For direct experimental study only those reactions are suitable that take place slowly, so that the system may be analyzed at intervals of 10 minutes, 30 minutes, 60 minutes, or longer, according to the nature of the reaction, and in that way data obtained from which to calculate the rate of reaction so as to express it in whichever of the two forms one prefers.

Many reactions take place so slowly that they can be studied directly in the way just indicated. Many others take place so rapidly that the rate cannot be measured directly. In such cases it might seem that it is not important to know the rate of the reaction. To a considerable extent that is true. Just as, in the case of very slightly soluble compounds, it may not be necessary to know the actual solubility if it is so low that the

amount remaining in solution can be disregarded. But in the case of two very slightly soluble compounds it may be very desirable to know which is the less soluble, and even something of the relative solubility of the two in order to carry out certain separations. So, in the case of reactions that take place very rapidly, it may not be necessary to know the actual rate, if it is so high that the reaction is complete in a short time; but it may be very desirable to know the relative rates of two reactions. Fortunately there are ways in which the ratio of two such rates may be calculated even though the individual rates cannot be measured directly. This will be referred to again under the subject of reversible reactions, where its more important applications are found (§11).

The concept of concentration involves the two ideas quantity and volume. It may be expressed in units showing the quantity present in unit volume or the volume necessary to contain unit quantity. The former is more commonly used, but the second form is found in such statements as, "a test is delicate to one part in two hundred and fifty thousand." In chemistry the unit of volume is one liter, and the unit of quantity is one gram molecular weight (or one mole). Unit concentration in this system is called a molar solution.[1] Thus, a molar solution is one which contains

[1] Besides the molar solution, several other systems are used for special purposes to indicate the concentration of reagents; such as the percentage solution, the empirical solution, and the equivalent-normal solution.

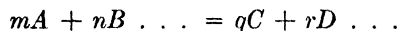
By definition a 10% solution should be one containing 10 g. of the substance per 100 g. of solution, or 10 cc. of the substance per 100 cc. of solution. In the laboratory, however, it is common practice to make up what is called a 10% solution by dissolving 10 g. of substance in a solvent and diluting to 100 cc. Not infrequently the worker neglects to take into account the presence of impurities, water of crystallization, etc., in weighing the available material. Thus various abuses have crept into the percentage system of expressing concentration so that the label, 10% solution, is meaningless unless one knows the particular plan followed.

The empirical solution is one in which the concentration has been so adjusted that 1 cc. of the reagent will carry out a convenient amount of change in another substance. Thus a potassium permanganate solution might be of such a strength that 1 cc. of it would oxidize 1 mg. of iron from the ferrous to the ferric condition. On that basis if a 0.1 g. sample were being analyzed, the number of cubic centimeters of permanganate solution required to oxidize the iron would be the per cent of iron in the sample. If a 1.0 g. sample were used, each cubic centimeter of permanganate would represent 0.1% of iron. This simplifies such calculations very much, and such a reagent is very useful when it is being used for only one such determination. If it were employed for several other determinations, however, then a separate "factor" would be required in each of the other cases, and the convenience of the reagent would disappear unless individual solutions were made up of different concentrations, one for each of the different determinations, or the weights of the samples taken were so adjusted that 1 cc. of the reagent would correspond to 1% of the constituent being determined.

The equivalent-normal solution (commonly called a normal solution) is most widely used in volumetric analysis, because of the 1:1 relation of reagents to each other in this system. A normal solution is one which contains 1 g. equivalent of substance per liter. Thus 20 cc. of 0.1 *N* NaOH will exactly neutralize either 20 cc. of 0.1 *N* HCl or 20 cc. of 0.1 *N* H_2SO_4.

one gram molecular weight (one mole) of substance per liter. For example: a molar solution of hydrochloric acid contains 36.5 g. (using 1 and 35.5 respectively for the atomic weights of H and Cl, one mole of HCl = 36.5 g.) of hydrogen chloride in a liter of solution.

The fact that the rate at which a reaction takes place depends in part upon the concentrations of the reagents is of profound importance, because the chemist can change the concentrations of reagents more or less at will and thus modify the rate of a reaction to suit his needs. Clearly, it would be especially helpful if a mathematical relationship could be established between the change in rate and the change in concentrations of the reagents. The earlier experimental studies along this line made it appear at first as if there might be a fairly simple relation between the two. In reactions involving only one molecule of the reagent in the balanced equation, the rate of the reaction was found to vary nearly directly with the concentration of the reagent. If the reaction involved two molecules of the reagent, the rate varied approximately as the square of the concentration of the reagent; while if three molecules of the reagent were involved the rate varied as the cube of the concentration of the reagent. These results led to the enunciation of the **Law of Mass Action,** which states that *the rate of a reaction varies as the active mass of each reagent raised to a power numerically equal to the coefficient of the reagent in the equation for the reaction.* Expressed mathematically, if the equation for the reaction reads:

$$mA + nB \ldots = qC + rD \ldots$$

the rate of the reaction will vary as $[A]^m \times [B]^n \ldots$ etc., in which $[A]^m$ means the active mass of A raised to the mth power, etc. For purposes of approximation, and particularly in dilute solutions and for weak electrolytes the active mass of a reagent may be considered as equal to the molar concentration of the reagent. On this basis the law of mass action is frequently stated in the following form: The rate at which a reaction takes place varies as the concentration of each reagent, raised to a power numerically equal to the coefficient of the reagent in the equation for the reaction.

In the case of rates of reaction, a basic quantity might be measured, namely, the normal or specific rate of the reaction. This would be the rate at which the reaction takes place (under definite conditions otherwise) when the concentrations of the reagents are all molar. If this normal rate, which depends on the specific character of the reagents themselves and on the other fixed conditions (temperature, pressure, catalyst, etc.) is represented by the letter k, then the mathematical expression for the Law of Mass Action becomes

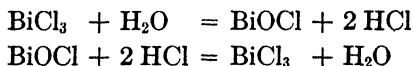
$$R = k \times [A]^m \times [B]^n \ldots$$

in which R is the actual rate of the reaction.

This conclusion might have been reached through the study of the laws of chance or probability. As a matter of fact, these laws helped very much to interpret the experimental data, and were largely responsible for the general acceptance of the Law of Mass Action as a law. Curiously enough, it was hardly well established as a law before more extended experimentation showed that in some cases the law, in its approximate form, deviated considerably from the truth. As is typical in such a situation, the generalization was still regarded as a law, but operating only in ideal cases. Within certain ranges of concentration most reactions are in accordance with the law; outside of these ranges experimental studies may lead to the finding of numerical factors which can be introduced to lessen the difference between experimental and calculated results. The study of the irregularities or deviations from ideal cases has led to a considerable extension of our knowledge of the chemistry of particular substances. It has also cleared up to a considerable extent the anomalous behavior of strong electrolytes.[1] The matter is too involved, however, to warrant discussion at this time.

§11. Reversible Reactions. — When the attempt was first made to account for the occurrence of chemical reactions in terms of relative affinities of elements and radicals for each other, it was found that certain annoying irregularities developed. That is, they were considered annoying at the time because they interfered with the development of the doctrine of Chemical Affinity into a universal explanation of chemical reactions. How simple it would have been if a table of chemical affinities could have been prepared so that all one needed to do was to consult the table to find out which reactions would take place and which would not! But actual experience proved to be less simple than that, and a better understanding of experimental fact was derived from further study of the irregularities.

The irregularities were of this sort: if a solution of bismuth chloride is treated with water, a precipitate of bismuth oxychloride is formed; but if this precipitate is treated with hydrochloric acid it dissolves, forming bismuth chloride again. The difficulty appears very clearly when the equations for these two reactions are written.

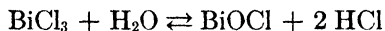
$$BiCl_3 + H_2O = BiOCl + 2\,HCl$$
$$BiOCl + 2\,HCl = BiCl_3 + H_2O$$

On comparing these two equations it is found that the reagents of the first reaction are the products of the second, and the reagents of the second are the products of the first. It is evident that in such a situation there must be more to chemical reactions than chemical affinity, for if one con-

[1] Hammett, Solutions of Electrolytes, McGraw-Hill, 1929, preface p. VI; Stieglitz, I, 108 et seq.

sidered these two reactions separately on the basis of chemical affinity alone it would be necessary to make statements of relative affinities to account for the first that would be exactly opposite to those that would be called for by the second.

At first these cases were set aside in a general group labelled "exceptions." But as reactions were studied more carefully the number of these exceptions became so great that something had to be done about them. They occur everywhere in chemistry; not only in aqueous solutions with which this book deals so largely, but in non-aqueous solutions (with which organic chemistry deals very extensively) and in gaseous reactions as well. Thus, anhydrous acetic acid reacts with anhydrous ethyl alcohol to form ethyl acetate and water; ethyl acetate reacts with water to form ethyl alcohol and acetic acid. Iron oxide heated in hydrogen forms metallic iron and water vapor; metallic iron heated in water vapor forms iron oxide and hydrogen. Hydrogen iodide on heating decomposes into hydrogen and iodine; hydrogen and iodine on heating combine to form hydrogen iodide. In each of these cases if the equations for the two reactions are written it will be found that the same relation exists between them as was pointed out in the case of the bismuth reactions above. In these pairs of reactions, the reagents of each reaction are the products of the other.

The name *reversible reaction* has been applied to any set of reactions of the type just described. To simplify the writing of the equations it has become common practice in these cases to combine the two equations into one, writing the formulas for the various materials only once and using two arrows pointing in opposite directions instead of the equals sign. The arrows mean that two equations are shown, one being read in the conventional way from left to right, the other being read in the opposite way, from right to left. Thus the two equations for the bismuth reactions may be written:

$$BiCl_3 + H_2O \rightleftarrows BiOCl + 2\,HCl$$

The fact that such a system is commonly spoken of in the singular as a reversible reaction, and is apparently represented by a simple equation, frequently leads the beginner into certain misunderstandings. Thus he sometimes gets the notion that a reversible reaction is an individual thing that can move back and forth much as a pendulum can swing to and fro. The practice of saying that such a reaction goes from left to right or from right to left accentuates this misconception. As a matter of fact the word "direction" used with reference to a reversible reaction is highly figurative. In the actual reaction, taking place in a beaker or test tube, there is no direction in which the reaction is taking place. If anything, the reaction is taking place in all directions at the same time. But if one writes the equations for the two reactions in the ordinary way with double arrows, then one may distinguish between the two by speaking of the reaction which

is read from left to right and the reaction which is read from right to left. Since it is purely arbitrary which one is written from left to right, such a method of distinguishing between the two applies only to the particular order of reagents and products in a given case. If the equation has been written then the statement that the reaction is taking place from left to right means merely that the reaction is taking place whose equation is read from left to right, or it may mean that this reaction is taking place faster than the one whose equation is read from right to left. It would be better if the figurative language were abandoned and the actual reactions discussed.

The fundamental thing is to realize that *a reversible reaction consists of two reactions which are so related to each other that the reagents of each are the products of the other.* In such a situation it becomes very important to know something of the relative rates at which the two reactions are taking place. This involves the law of mass action, so the next topic to be discussed is the application of the law of mass action to reversible reactions.

§12. The Law of Mass Action Applied to Reversible Reactions. — The law of mass action is considered to be a general law, showing the way in which the rate of a reaction varies with the concentration of each reagent. On that basis, on the instant of mixing the reagents their concentrations will be greatest and the rate of the reaction will have its maximum value. As the reaction proceeds the reagents are being used up and the rate of the reaction falls off. The rate steadily decreases as the concentrations of the reagents decrease, but so far as mathematical calculation goes, the reaction will never be complete because the lower the concentration of the reagents the slower the rate at which the reaction takes place. Practically, of course, if one is satisfied with an accuracy of 0.1%, then it is necessary to continue the reaction only until it is 99.9% complete. If the reaction is an irreversible one of the fast type this may require from several minutes up to several hours. If it is a slow reaction it may take many years to even approximate that sort of completeness. In expressing the rate at which radioactive substances decompose, it frequently becomes necessary to resort to "half-life periods" in order to give the figures practical meaning. The half-life of a radioactive element is the time necessary for the material to undergo 50% decomposition. Some instances are given in Table 3.

In the case of reversible reactions the situation is complicated by the fact that not only will the reaction take place which one wishes to carry out, but another reaction will also take place which is just the opposite of the one desired. Further, according to the law of mass action, the rate of the interfering reaction will increase as more and more of the desired products are formed. Sometimes by setting up certain conditions of temperature and pressure it is possible to prevent the reverse reaction from interfering seriously, but frequently both reactions are affected in a similar way

by such external conditions or there are practical difficulties in establishing and maintaining these conditions, and in such cases it is necessary to search for other ways out of the trouble.

TABLE 3

HALF-LIFE PERIODS OF SOME RADIOACTIVE SUBSTANCES

Substance	Half-life period
Actinium A	0.002 second
Niton	3.85 days
Radium	2000 years

The extent of the interference depends on the specific rates of the two reactions. If the specific rate of the first reaction is the same as that of the second then the best yield that can be obtained by mixing equivalent amounts of the reagents will be 50%. If the specific rate of the first is nine times that of the second then the best yield that can be obtained by mixing equivalent amounts of the reagents will be 90%. In irreversible reactions it is merely a matter of time to obtain any desired degree of completeness. In reversible reactions the figures given in the cases just cited are limiting figures which cannot be improved by merely waiting somewhat longer. They represent the best that can be done regardless of how long one waits, and in the actual case one usually accepts something less satisfactory in order to set a reasonable limit on the time of waiting. The reason for this situation is found in the setting up of a condition known as chemical equilibrium.

§13. **Chemical Equilibrium** is the condition reached when both the reactions of a reversible reaction are taking place at the same rate. Because of the special inter-relation of the two reactions, this means that the reagents of each reaction are being used up by interaction with each other just as fast as they are being formed as products by the other reaction. Under such conditions the concentrations of the reagents do not change; therefore, if the other conditions of the reactions are kept constant, the two reactions continue to maintain equal rates and to offset each other. If reaction I is started by bringing together the proper reagents it forms, as products, the reagents of reaction II. Under such conditions the rate of reaction I starts at a certain maximum and decreases as the reaction proceeds, while reaction II starts at a minimum and increases. So long as reaction I is taking place faster than reaction II the reagents of reaction I are being used up faster than they are being formed and the rate of reaction I continues to decrease, while the reagents of reaction II are being formed faster than they interact and the rate of reaction II continues to increase. With the rates changing in that way they are approaching each other in value

and it is only a question of time until they become equal. When they do become equal a condition of chemical equilibrium is reached which then maintains itself indefinitely.

Since a reversible reaction can be carried only to a condition of chemical equilibrium it is important to know something of the actual concentrations of the various materials that will be present when such a condition has been reached. Fortunately this information has been made available in the form of tables of *equilibrium constants*. If a particular reaction is of a type to be represented by the equation, $A + B \rightleftarrows C + D$, then, when chemical equilibrium has been set up and the two reactions are taking place at the same rate, R_1 (the rate of reaction I) $= R_2$ (the rate of reaction II) and, since $R_1 = k_1 \times [A] \times [B]$ and $R_2 = k_2 \times [C] \times [D]$, then $k_1 \times [A] \times [B] = k_2 \times [C] \times [D]$. In this expression k_1 and k_2 are the specific rates of reactions I and II (when the reagents are present in unit concentrations) and $[A]$, $[B]$, $[C]$ and $[D]$ are the actual concentrations of A, B, C and D. The last mathematical equation may be rearranged as follows:

$$\frac{[C] \times [D]}{[A] \times [B]} = \frac{k_1}{k_2} = K$$

Since the concentrations do not change so long as equilibrium is maintained it is evident that the concentrations have adjusted themselves in such a way as to show a constant ratio of product of concentrations of products to product of concentrations of reagents. This ratio is numerically equal to the ratio of the specific rate of the first reaction to the specific rate of the second. Commonly, the ratio is called the equilibrium constant of the reaction and is represented by the letter K. If the equations were written in reverse order the value of K would then be the reciprocal of the one just indicated, so it is very important to know which substances belong in the numerator and which in the denominator before using the numerical values for equilibrium constants. Further, since reaction rates are usually affected by changes of temperature, the value for an equilibrium constant can be used only for the particular temperatures at which it applies.

In determining equilibrium constants two methods are available. If the reactions proceed slowly enough so that their rates may be determined, the specific rates may be calculated and thus the ratio of specific rates obtained. If the reactions take place so rapidly that the rates cannot be measured directly, it will still be possible to determine the equilibrium constant if it is possible to measure accurately the concentration of any one of the reagents or products, after equilibrium has been set up and without disturbing the condition of equilibrium. This usually requires an indirect method. In such a case the reagents may be mixed in definite proportions, the reaction permitted to come to equilibrium, and the concentration of this one substance measured. From the equation for the reaction involved, the concentrations mixed at the start, and the con-

centration of this one substance when equilibrium is reached, the concentrations of the other substances can be calculated and thus the equilibrium constant determined. In reactions in aqueous solutions the second method is more commonly employed.

The statement was made above that the best one can do is to reach a condition of chemical equilibrium. This is true, but it is equally true that so long as equilibrium has not been reached one of the reactions is taking place faster than the other. The law of mass action provides an invaluable means of making it possible for many reactions to take place to a sufficient extent to satisfy our needs before conditions of chemical equilibrium are reached. If in such a reaction as $A + B \rightleftarrows C + D$, it is especially desired to use up B as completely as possible, it may be feasible to start with more than an equivalent amount of A, so that there will be a higher initial rate of interaction between A and B; and the reaction will use up B to a greater extent before equilibrium is reached than if only an equivalent amount of A were used. On the other hand it may be desirable to get A used just as completely as B. In that case it may be possible to manipulate the concentrations of C and D in such a way as to accomplish this. If conditions may be arranged by the use of temperature, pressure, accessory reagents or solvents to keep the concentration of either C or D (or both) very low then the rate of interaction between C and D may be kept so low that the reaction between A and B can take place to the desired extent before reaching equilibrium. In both of these cases the law of mass action is being used. If one uses the phrase "normal concentrations of materials" to mean those that exist when equilibrium is reached after starting with equivalent quantities of the reagents, then the concentration of either reagent may be made abnormally low by use of excess of the other reagent or by keeping the concentration of either product abnormally low. The effectiveness of either of these means depends upon the ratio of the concentration of reagent used to the normal concentration (as above defined), and upon the ratio of the normal concentration of the product to the actual concentration established in the reaction. Thus, increasing the concentration of the reagent tenfold produces a greater effect than only doubling it, and decreasing the concentration of a product to one-tenth its normal value has a greater effect than only reducing it to one-half. There are practical limits to the extent to which the concentration of a reagent can be increased, but the concentration of a product may be decreased indefinitely, and so in actual practice the second method of controlling a reversible reaction is commonly the more effective. Thus a saturated solution of hydrogen chloride in water is only 12 N so this is the upper limit of concentration of hydrochloric acid that can be had in an aqueous solution, but by evaporating a solution of hydrochloric acid with excess of sulfuric acid it is possible to lower the concentration of hydrochloric acid in the solution to zero. The effective concentration of hydrochloric acid can

only be increased one hundred and twenty fold by substituting 12 *N* hydrochloric acid for 0.1 *N* hydrochloric acid, but it can be decreased one million fold by evaporating with sulfuric acid until its concentration has been reduced to 0.000,000,1 *N*.

Since the reactions employed in qualitative analysis are largely reactions in aqueous solution, the detailed applications of the law of mass action to reversible reactions will be made only to that type of reactions (§16). It should be remembered, however, that this is only a limited group of reactions and that the law of mass action applies to all reactions, ionic and non-ionic, reversible and irreversible.

It is instructive to note that the relation of the law of mass action to chemical equilibrium is such that one might study either one experimentally and derive the other by inference. Thus, granted that one is acquainted with the law of mass action through study of reaction rates and that one knows of such things as reversible reactions it requires only a logical application of the law to the two reactions of such a system to realize that a condition of chemical equilibrium is the obvious state to be reached if both reactions are taking place. Or, if one is acquainted experimentally with the fact of chemical equilibrium in reversible reactions the attempt to find an explanation for this leads inevitably to the law of mass action. According to the way in which the law is derived it is sometimes spoken of as "The Mass Action Law of Reaction Rates," and sometimes as "The Mass Action Law of Chemical Equilibrium."

REACTIONS OF INORGANIC SUBSTANCES IN AQUEOUS SOLUTIONS

§14. Water as Solvent and as Reagent. — The reactions used in qualitative analysis are chiefly the reactions of inorganic acids, bases and salts with each other in aqueous solution. It is necessary to have a reasonable understanding of the conditions actually existing in such solutions in order to correlate the large number of individual reactions actually encountered and to understand how they may be manipulated and controlled to serve certain purposes. There is danger of forgetting that these reactions are carried out in the presence of relatively large amounts of water. Sometimes the water serves in the rôle of catalyst, as solvent to cause much more intimate contacts of the two reagents than are possible by ordinary grinding or mixing together, thus bringing about the molecular collisions that seem necessary to produce reactions. Sometimes the water enters into the re-

action as an obvious reagent, as in reactions involving hydrolysis. Thus in the precipitation of ferric hydroxide by adding sodium carbonate solution to a solution of ferric chloride, the hydroxyl ion is derived from the water and not from the sodium carbonate although the sodium carbonate is involved in making hydroxyl ion available.

§15. **The Theory of Ionization.** — The most important aid in understanding this class of reactions is found in the theory of ionization. It was developed originally as an explanation for irregularities in the behavior of aqueous solutions as compared with non-aqueous solutions and even among aqueous solutions themselves. These irregularities had to do with certain physical properties that are commonly measured in the determination of approximate molecular weights, namely the boiling points and freezing points of solutions of known concentration as compared with the boiling point and freezing point of the pure solvent. These irregularities are also found in studying the osmotic pressures of the different solutions, but the experimental difficulties of accurate osmotic pressure measurements are so great that this type of study is seldom made.

The case of boiling points and freezing points may be stated very simply. A pure solvent boils at a definite temperature when the gas pressure above it is fixed. If the gas pressure is 760 mm. (atmospheric pressure) the temperature at which the liquid boils is called its boiling point. In the same way a pure solvent freezes at a definite temperature, which is affected so slightly by pressure that it is unnecessary to specify the pressure in ordinary work. The temperature at which the liquid freezes is called its freezing point. These temperatures are so definite that they are commonly used to identify particular liquids. If a solute is added to a solvent the boiling point of the solution is found to be higher than that of the pure solvent and the freezing point of the solution is lower than that of the pure solvent. In the normal case the changes in boiling points and in freezing points are directly proportional to the number of moles per 1000 g. of solvent.[1]

[1] It will be noted that this solution is not quite the same as a molar solution, which is defined as one containing 1 mole of solute per liter of solution. In concentrated solutions the difference between the two may be considerable, but in dilute solutions it is negligible. This may be seen by comparing the data for three sodium chloride solutions.

Sp. Gr. of Soln.	g. NaCl per liter	Moles per liter	Moles per 1000 g. of H_2O	Ratio $\frac{\text{col 4}}{\text{col 3}}$
1.1640	256.1	4.378	4.822	1.101
1.0413	62.48	1.071	1.094	1.021
1.0053	10.05	0.1718	0.1728	1.006

The fact that in dilute solutions the ratio in the last column is approximately 1, has frequently led to the calculation of data in terms of moles per liter instead of moles per 1000 g. of solvent.

This makes it possible to determine the boiling point or freezing point of a solution containing one mole of solute in 1000 g. of solvent, compare this value with the boiling point or freezing point of the pure solvent, and by difference obtain quantities which are called "the molar raising of boiling point" and "the molar lowering of freezing point" of the solvent. Thus the molar elevation of boiling point of water is 0.52, and the molar depression of freezing point of water is 1.86. This means that if an aqueous solution of a given substance boils at 100.52° under standard atmospheric pressure, or freezes at −1.86°, it contains one mole per 1000 g. of water. If the concentration is known in grams per 1000 g. of water, that number will be the molecular weight of the substance. If the solution boils at 100.26° or freezes at −0.93° it contains 0.5 mole per 1000 g. of water, and the concentration in grams per 1000 g. of water must be multiplied by two to obtain the molecular weight. On that basis the molecular weight of a substance may be determined by preparing a solution of known concentration in grams per 1000 g. of water, determining its boiling point or freezing point, and from the corresponding figures for the pure solvent and the boiling point elevation or freezing point depression characteristic of the solvent calculate the molecular weight of the solute.

The above is the usual case. In organic chemistry it supplements in a very valuable way the information derived from analysis, both confirming the analysis and making it possible to distinguish between polymers of the same chemical analysis. In aqueous solutions, however, many cases are encountered which are decidedly irregular. In fact the ordinary inorganic acids, bases and salts, the very materials with which qualitative analysis deals almost exclusively, show irregularities to varying extents.

A typical substance to illustrate the experimental data is sodium chloride. According to the atomic weights of sodium and chlorine (23.0 and 35.5 respectively) and the molecular formula, NaCl, the molecular weight should be 58.5. But when the salt is tested the freezing point of a solution containing 58.5 g. per 1000 g. of water is not the normal freezing point of a

TABLE 4

APPARENT MOLECULAR WEIGHTS OF NaCl FROM FREEZING POINTS OF SOLUTIONS

Concn. of soln. g./1000 g. H_2O	Freezing point of soln.	Apparent mol. wt.
58.5	−3.35°	32.5
29.25	−1.70	32.0
5.85	−0.36	30.2

solution containing one mole per 1000 g. of water, nor is the lowering of freezing point of water by various amounts of sodium chloride directly proportional to the number of moles per 1000 g. of water. This is shown in Table 4.

Another salt, magnesium sulfate, gives a freezing point for a solution containing 0.5 mole per 1000 g. of water from which a molecular weight would be calculated only 92% of the correct value, while a solution containing 0.01 mole per 1000 g. of water leads to a number only 61% of what it should be.

In finding an explanation for these irregularities the theory of ionization was developed. In the ordinary or regular case the direct connection between the number of moles of solute per 1000 g. of solvent and elevation of boiling point or depression of freezing point is explained by assuming (1) that the change in boiling point or freezing point is brought about by dissolved particles in the solution, (2) that the magnitude of the change is directly proportional to the number of particles of solute in a given amount of the solvent, and (3) that in the ordinary solution these particles are really molecules of the solute. All molecules are considered to have equal capacity to produce this effect, therefore solutions containing the same number of moles of solute per 1000 g. of solvent, should show the same elevation of boiling point or depression of freezing point for a given solvent. In the irregular case the general assumptions are the same except the last one. Here it is assumed that there may be some splitting of molecules into smaller particles each of which is able to produce the same sort of effect as the molecule would. Since this forms a larger number of particles than would be found if the solute were all present as molecules, the elevation of boiling point or depression of freezing point of the solvent should be abnormally great. Conversely, since the molecular weight calculated is merely the average molecular weight of the particles present it will be lower than the true molecular weight of the compound dissolved. The actual extent to which a given compound will produce deviations from normal boiling point or normal freezing point will depend both on the relative number of molecules that are split in this way, and on the number of particles into which each molecule splits. Thus, if all the molecules split into two particles each, the boiling point should be raised and the freezing point lowered just twice as much as if the particles were all molecules. If three particles were obtained from one molecule and the molecules were all dissociated the effects would be three times the normal effect and the apparent molecular weight would be one third the true molecular weight.

Individual compounds show their own characteristic extents of dissociation, ranging in ordinary solutions practically all the way from zero to one hundred per cent. On the basis of the assumption that these simpler particles — or ions, as they are called — have exactly the same ability to raise the boiling point or lower the freezing point as the same number of molecules, it is easy to calculate the extent of dissociation of a compound in a particular solution from the boiling point or freezing point data.

Let n = no. of molecules if no dissociation took place

a = no. of molecules dissociating

2 = no. of ions obtained from each molecule that dissociates

Then $\frac{a}{n}$ = extent of dissociation

$n - a$ = no. of molecules of solute present

$2a$ = no. of ions present

$n + a$ = no. of particles present (molecules + ions)

$$\frac{n + a}{n} = \frac{\text{actual depression of freezing point (or elevation of b.p.)}}{\text{normal depression of freezing point (or elevation of b.p.)}}$$

$$\frac{a}{n} = \frac{(\text{actual dep. of f.p.}) - (\text{normal dep. of f.p.})}{\text{normal dep. of f.p.}}$$

Using the data above for sodium chloride, in a solution containing one mole per 1000 g. of water, the freezing point depression is 3.35° C. The normal depression for water is 1.86° on the Centigrade scale. Then the extent of dissociation of the sodium chloride is $\frac{3.35 - 1.86}{1.86} = 0.80 = 80\%$. In a solution containing one-tenth of a mole per 1000 g. of water the sodium chloride is calculated to be 94% dissociated.

The significance of all this so far as chemical reactions are concerned is this: many physical and chemical properties of the solutions are effectively understood by correlation with the concept of ionization in solution. Thus the fact of electrical conductivity of solutions is accounted for by assuming that the ions are charged electrically, and the whole electro-chemistry of aqueous solutions is built around the electric properties of the ions. In this connection it may be interesting to point out that conductance measurements can be made more easily and with greater accuracy than boiling point or freezing point determinations and have been used extensively to obtain data from which to calculate extents of dissociation. It is particularly valuable for those cases where the extent of dissociation is very slight. The reasoning involved will not be developed here, but it is intimately connected with material presented in the next topic which deals with the law of mass action as applied to ionic reactions (§19).

The theory that ionization occurs in aqueous solutions is so widely accepted that it no longer requires detailed justification. In fact it is hardly to be considered a theory, but deserves to rank with the other important categories by which chemical facts are classified. The ions are considered to be chemical substances capable of taking part in all kinds of chemical reaction: combination, decomposition, complex formation, oxidation, reduction, etc. This means that the ordinary chemical reagent is a fairly complex system. A solution of hydrochloric acid instead of consisting

merely of hydrogen chloride in the presence of a solvent contains all of the following chemical substances: hydrogen chloride, hydrogen ion, chloride ion, water, and hydroxyl ion. This is the shortest list that can be written to account for the various chemical properties of the reagent. Evidence is accumulating which shows that the list may need to be extended. Each of the substances listed has its own specific chemical properties which will be manifested to a large or slight extent according to its concentration. The chemical properties of such a reagent are the sum total of the chemical properties of the individual substances present, those being most pronounced, of course, which are due to materials present in relatively large amounts. Thus the fact that lead chloride precipitates readily on treatment of a lead nitrate solution with calcium chloride, but not with mercuric chloride, is accounted for by the difference in concentrations of chloride ion supplied by the two reagents. This checks well with the experimental data concerning the extent of dissociation of the two salts in aqueous solution. The fact that silver chloride is formed by reaction of silver nitrate solution with sodium chloride but not with sodium chlorate is accounted for by the further fact that the reaction depends upon chloride ion, which is supplied by the sodium chloride but not by the sodium chlorate.

The theory of ionization is not yet in its final form. Even the first workers in the field recognized the fact that in its original form it did not offer an adequate explanation for all the diverse facts of aqueous solutions of electrolytes. In the earlier stages, however, intensive study was confined largely to the study of cases in which the theory worked well, in which results of experiment were checked by results calculated by application of the theory. In that way the theory was developed into a comprehensive scheme that dealt with a large range of information very nicely. The cases that didn't work were temporarily set aside as irregular or anomalous. As more and more of these were recognized it became evident that the two general classes of electrolytes, (1) those that fit into the system and (2) those that do not, are the weak electrolytes and the strong electrolytes, respectively. It now appears that the strong electrolytes as a group can be considered more simply in terms of the assumption that they are for practical purposes completely ionized in solutions of ordinary concentration. It is easier to account for apparent changes in extent of ionization of sodium chloride in different concentrations of solution by reference to the electrical properties of the ions than it is to account for the failure of the law of mass action to predict the apparent extent of ionization in particular concentrations of solution. At present the two classes of substances usually are dealt with separately, and the intermediate compounds which are only moderately irregular are in a third class to which neither set of rules apply exactly, but which may be treated as approximations to either.

It may be interesting to note that while the anomalous behavior of strong electrolytes was long used to discredit the theory of ionization, the recent

developments have only established the theory more strongly. The difficulty was that the experimental irregularities on which the theory was originally based did not account for as much ionization as is now believed to take place in the case of the strong electrolytes. This may mean merely that the secondary assumption, that the ions have the same ability to produce these effects as do the molecules, is only an approximation instead of an exact relation. In the case of the weak electrolytes the error introduced by considering it an exact relation is slight because the relative number of ions is small. In the case of the strong electrolytes the error is greater as the relative number of ions becomes large. Further, the freedom of the ions changes with the number of ions in the solution, due to forces of attraction and repulsion that are set up.

§16. **The Law of Mass Action Applied to Ionic Reactions.** — Ions are chemical substances. They are capable of reacting not only with other ions but with all types of other chemical substances. The term, ionic reaction, is used to cover any reaction which involves one or more ions either as reagent or product. Ionic reactions are typical reversible reactions to which all the material applies that was given under the topics, reversible reactions, and the law of mass action applied to reversible reactions. Under the latter topic it was stated that some of the detailed applications would be given in connection with ionic reactions. These will now be discussed.

§17. **Ionization Constants.** — One of the very interesting types of ionic reactions is ionization, itself. Ionization is the splitting of molecules into ions. This is a reversible reaction, so that in the ordinary reagent two reactions are taking place, (1) the dissociation of molecules into ions, (2) the combination of ions into molecules. When a particular extent of dissociation exists in a certain concentration of an electrolyte, this merely means that a condition of chemical equilibrium has been established, that the concentrations of molecules and of ions have so adjusted themselves that the two reactions are taking place at the same rate. There should be an equilibrium constant characteristic of the reversible reaction. Many such constants have been calculated from experimental data. They are called the ionization constants, or dissociation constants, of the compounds undergoing dissociation. Thus, the ionization constant of ammonium hydroxide is 0.000018 at 18°. Since temperature changes usually affect the extent of dissociation of an electrolyte, the values of ionization constants apply only for the particular temperatures at which the experimental data were obtained.

In calculating ionization constants it should be possible, theoretically, to start either with data on the specific rates of the two reactions or with data on the concentrations of ions and molecules at equilibrium. Prac-

tically, ionic reactions take place so rapidly that there is no direct way to measure the reaction rates, therefore it is necessary to use the second method. If data are at hand showing the extent of dissociation of the compound in a solution of known concentration the calculation of the ionization constant is easy.

Problem. Given the information that ammonium hydroxide is 1.34% dissociated in 0.1 *M* solution, calculate the ionization constant of ammonium hydroxide.

The general formula for equilibrium is written:

$$\frac{[NH_4^+] \times [OH^-]}{[NH_4OH]} = K$$

in which

$[NH_4^+]$ is the molar concentration of ammonium ion

$[OH^-]$ is the molar concentration of hydroxyl ion

$[NH_4OH]$ is the molar concentration of undissociated ammonium hydroxide

If the ammonium hydroxide is 1.34% dissociated, 98.66% is in the molecular or undissociated form. If the total concentration of ammonium hydroxide (both ionized and non-ionized) is 0.1 *M* then:

$$[NH_4^+] = 0.0134 \times 0.1 = 0.00134\ M$$
$$[OH^-] = 0.0134 \times 0.1 = 0.00134\ M$$
$$[NH_4OH] = 0.9866 \times 0.1 = 0.09866\ M$$

Substituting these values in the above formula,

$$K = \frac{0.00134 \times 0.00134}{0.09866} = 0.0000182$$

If such a number is to be of value in chemistry it should be characteristic of the reversible reaction when equilibrium has been reached regardless of the particular concentrations of the substances. Thus, the experimental data for molar or hundredth molar solution should lead to the same value for *K*. That it really does this is shown by Stieglitz[1] in the case of acetic acid. Experimental data for four concentrations of acetic acid gave the following results:

TABLE 5

IONIZATION CONSTANTS FOR ACETIC ACID

Molar concn. of acetic acid	*K*
0.1	0.0000182
.08	.0000183
.03	.0000185
.01	.0000181

In the case of strong electrolytes the attempt to use the ordinary experimental data to calculate ionization constants results in failure, as may be seen from the data on potassium chloride solutions in Table 6.

[1] Stieglitz, I, 99.

It is obvious that a ratio which varies nearly fourfold in a tenfold change of concentration cannot be considered as a constant. Empirically it has been observed that there is a distinct similarity in the irregularities noted when the electrolytes are of the same valence type. The valence types referred to are (1), uni-univalent electrolytes ($AB \rightleftarrows A^+ + B^-$), (2), uni-bivalent or bi-univalent electrolytes ($A_2B \rightleftarrows 2\,A^+ + B^{--}$, or $AB_2 \rightleftarrows A^{++} + 2\,B^-$), etc. The irregularity is even more marked with higher valence

TABLE 6

IONIZATION RATIOS FOR POTASSIUM CHLORIDE

Concentration M	Ionization %	Ratio $\frac{[K^+] \times [Cl^-]}{[KCl]}$
0.1	86.1	0.533
.05	88 5	.341
.01	94.3	.156

types than with the lower valence types. For many years the strong electrolytes were merely classed as irregular or anomalous in their behavior. More recently, however, the interionic attraction theory has made the valuable suggestion that in the electrical environment set up in the solution of a strong electrolyte the individual ions are subjected to a restraint such that they exert less than a normal effect on the physical properties of the solution from which extents of ionization are calculated. On that basis, the compound is considered to be more highly ionized than would be calculated from the experimental data. Thus mathematical calculations have shown that if the strong electrolytes are assumed to be practically completely ionized, the electrical effects would produce approximately the variations in apparent extent of ionization actually observed for the various valence types. It is becoming common practice, therefore, to assume complete ionization of the strong electrolytes in ordinary ranges of concentration rather than to use the figures that have been calculated from the usual data.

In the case of weak electrolytes, however, the above figures for acetic acid are typical, demonstrating a reasonably constant value for K over a considerable range of concentrations. With such concordance of values calculated from different experimental data, it should also be possible to calculate the extent of dissociation of such a compound at any particular concentration from the ionization constant of the compound.

Problem. If K_{NH_4OH} is 0.0000182, what is the extent of dissociation of ammonium hydroxide in 0.5 M solution?

Let x = extent of dissociation of the ammonium hydroxide.

Then $[NH_4^+] = 0.5x$

$[OH^-] = 0.5x$

$$[NH_4OH] = 0.5\ (1 - x)$$

$$K = \frac{[NH_4^+] \times [OH^-]}{[NH_4OH]} = 0.0000182^{1} = \frac{(0.5x)(0.5x)}{0.5\ (1 - x)}$$

Simplifying,

$$\frac{x^2}{1 - x} = 0.0000364$$

$$x = 0.006 = 0.6\%,$$

the extent of dissociation of ammonium hydroxide in 0.5 M solution.

§18. **Common Ion Effect.** — In ionic reactions the common ion effect is frequently spoken of and still more frequently used. It is a practical application of the law of mass action. In an ionic reaction the concentration of a particular ion can be increased by the addition of a compound that produces that ion on dissociation. The term common ion refers to the fact that this particular ion is derived from the reagent added as well as from a compound already in solution, so that the ion may be spoken of as common to the two compounds. The effect of this is to produce in the solution a higher concentration of this ion than would be furnished by either of the two compounds alone. Under such conditions, equilibrium will be set up in the ionization of each of these compounds with the concentration of the molecular material higher and the concentration of the other ion lower than would be the case if the one ion were derived only from the one compound. That is, the compound is less ionized than it would normally be at the concentration in which it is present. The effect of common ion is spoken of as "repressing the ionization of a compound" or "preventing a compound from dissociating to its normal extent," according to whether (1) the ion is being added to a solution containing the compound already dissociated, or (2) the compound is being added to a solution containing the ion in question. Thus, if hydrogen chloride is added to a solution of hydrogen sulfide, the ionization of the hydrogen sulfide will be repressed; but, if hydrogen sulfide is added to a solution of hydrochloric acid, the hydrogen sulfide will

[1] In such problems certain mathematical aids are frequently employed. (1) In writing very small numbers several methods may be used.

$$0.0000182 = 0.0_4182 = 1.82 \times 10^{-5}$$

(2) If one number is very small as compared with another the sum or difference of the two numbers is approximately identical with the larger number so the larger number may be used in place of the sum or difference of the two with only slight error. This is useful to simplify certain mathematical steps. In the above case $\frac{x^2}{1 - x} = 0.0000364$. It is known that x is small as compared with 1 since ammonium hydroxide is only slightly dissociated. Therefore $1 - x$ is approximately equal to 1. Substituting 1 for $1 - x$ the expression becomes $x^2 = 0.0000364$. The slight amount of error thus introduced becomes evident only on carrying the value for x out to the third significant place. By exact mathematics, $x = 0.00602$, by the method of approximation, $x = 0.00603$. The difference is within the limit of experimental error and so is negligible.

be prevented from dissociating to its normal extent (i.e., to the extent that it would if there were no hydrochloric acid present). In so far as equilibrium conditions are concerned these should be the same which ever the order of mixing of the materials, but it makes an enormous difference in individual cases as to the readiness with which the desired conditions are set up. Thus it is much easier to obtain a solution with no zinc sulfide precipitated by adding hydrochloric acid to a solution of zinc chloride before treating with hydrogen sulfide than it is to treat the solution of zinc chloride with hydrogen sulfide and then add an amount of hydrochloric acid that should lower the concentration of sulfide ion to the same value that it has in the first solution.

The common ion effect decreases the extent of ionization of both the compounds involved. But the extent to which each compound is affected depends upon the ratio of the total concentration of the given ion to the concentration that would be supplied by the compound alone. If the total concentration is only slightly larger than that which the compound alone would furnish, the effect is slight and may be considered negligible; if the total concentration is very much larger than that which the compound alone would furnish, the effect is correspondingly marked and may be very important. This effect furnishes a highly valuable means for controlling the concentration of particular ions supplied by weak electrolytes. By application of the law of mass action it is possible, with the aid of the ionization constant of the weak electrolyte, to calculate the magnitude of the effect.

Problem. What is the extent of ionization of ammonium hydroxide in 0.1 M solution, containing ammonium chloride (0.5 M, completely ionized), if $K_{NH_4OH} = 0.0_418$?

$$\frac{[NH_4^+] \times [OH^-]}{[NH_4OH]} = K = 0.0_418$$

Let x = extent of ionization of the ammonium hydroxide, then

$$[NH_4^+] = 0.1x \text{ (from } NH_4OH) + 0.5 \text{ (from } NH_4Cl)$$
$$[OH^-] = 0.1x$$
$$[NH_4OH] = 0.1\ (1 - x)$$

Substituting in the above formula,

$$\frac{(0.5 + 0.1x)(0.1x)}{0.1\ (1 - x)} = 0.0_418$$

Simplifying by the method of approximation,

$$(0.5 + 0.1x) = \text{approximately } 0.5$$
$$(1 - x) = \text{approximately } 1$$
$$\frac{(0.5)(0.1x)}{0.1} = 0.0_418, \quad \text{or} \quad 0.5x = 0.0_418$$
$$x = 0.0_436 = 0.0036\%$$

the extent of ionization of ammonium hydroxide in a solution which is 0.1 M with respect to NH_4OH and 0.5 M with respect to NH_4Cl.

The extent of dissociation of NH_4OH in 0.1 *M* solution was given above as 1.34%. Comparing that figure with the present one shows that the presence of 0.5 *M* NH_4Cl reduces the extent of dissociation to 0.0027 what it would be in the absence of the NH_4Cl.

It may be worth while, for sake of emphasis, to show again that a method of approximation is justified in the above case and to indicate also that the effect of the ammonium hydroxide in repressing the ionization of the ammonium chloride must be entirely negligible.

If $x = 0.0_436$, then $(0.5 + 0.1x) = 0.5000036$, which differs from 0.5 by only one part in one hundred forty thousand, which is entirely beyond the range of accuracy of the experimental measurements. It is evident that the ammonium hydroxide does not increase the concentration of ammonium ion appreciably above that supplied by the ammonium chloride alone, therefore it could have only an inappreciable effect on the extent of ionization of the ammonium chloride. Further, according to the modern concept that the ammonium chloride is completely ionized, the effect of common ion on the extent of ionization of the ammonium chloride would be negligible even if it involved many fold increase in the concentration of the one ion. This apparent difficulty is realized more clearly if it is put into mathematical form. If a salt, such as ammonium chloride, is considered to be completely ionized, the concentration of molecular ammonium chloride is zero regardless of the concentration of the solution, and the ionization constant is

$$\frac{[NH_4^+] \times [Cl^-]}{0} = \text{infinity.}$$

Under such conditions a change in concentration of ammonium ion or chloride ion cannot change the concentration of molecular ammonium chloride, and therefore the ammonium chloride remains completely ionized. If it remains completely ionized the concentration of chloride ion should not change. On the other hand, if ammonium and chloride ions will react with each other, the rate of such reaction will vary as the concentration of each reagent. Therefore, doubling the concentration of ammonium ion should double the rate of reaction between the two, resulting in a lowering of concentration of chloride ion. These two conclusions can be reconciled in only one of two ways. Either the assumption must be made that the strong electrolytes are only largely dissociated into ions instead of completely ionized, in which case the dissociation constant has finite value and the above difficulty disappears; or there is no such thing as molecular or undissociated ammonium chloride, in which case there can be no such reactions as ammonium chloride dissociating into ions or ammonium and chloride ions combining to form ammonium chloride. Some of the modern chemists are inclined to advocate the latter view as a simple explanation for some of the experimental material in which they are interested; but

when a wider range of chemical fact is included it appears as if there is better chance for satisfactory progress with the first alternative suggested.

§19. **Dilution Effects.** — Another interesting fact about ionization, considered as a reversible reaction, is that the two reactions have unequal numbers of reagents. Thus, in the dissociation of ammonium hydroxide into ions there is only one reagent, while in the combination of ammonium ion and hydroxyl ion to form ammonium hydroxide there are two reagents. As a result of this it is possible to disturb chemical equilibrium in a solution of an electrolyte by either increasing or decreasing the amount of water present; that is, by increasing or decreasing the volume of the solution. If the volume of the solution is increased the concentration of each of the substances in the solution is decreased to a corresponding extent. Thus, if the volume of the solution is doubled, the concentration of each substance in the solution becomes half what it was. This means that, since the rate of dissociation of the molecules into ions depends upon the concentration of molecular material, the rate of dissociation becomes half what it was. But at the same time the concentrations of the ions have been decreased to half what they were, and, since the rate of combination of the ions varies as the concentration of each ion, the rate of combination of the ions becomes one-fourth what it was. (Considering the simplest case of two ions combining to form one molecule.) As a result the molecules are now dissociating faster than the ions are combining, a condition which leads to a further lowering of concentration of molecular material and something of an increase in concentration of the ions until the two reactions are again taking place at equal rates and a new condition of chemical equilibrium is set up. In this new state the proportion of ions to molecules is greater than before and therefore the compound is more highly ionized than it was before the solution was diluted. This is the explanation for the statement that diluting the solution of a compound increases its extent of dissociation.

It is easy to calculate the effect of diluting a solution a given amount on the extent of dissociation of a compound in the solution. This may be done either with the aid of the ionization constant of the compound or directly on the assumption that the law of mass action applies. In the problems on the ionization of ammonium hydroxide the first method is shown. The extent of ionization in 0.1 M solution being given, the ionization constant was calculated, and, from that, the extent of ionization in 0.5 M solution. The two values are 1.34% for 0.1 M, and 0.60% for 0.5 M solutions. The direct calculation is based on the following mathematical relation:

Let x = extent of dissociation of compound AB at concentration "a"
y = extent of dissociation of compound AB at concentration "b"

Then $\frac{(ax)^2}{a(1 - x)} = \frac{(by)^2}{b(1 - y)}$ for equilibria in the two concentrations of the compound.

$$\frac{x^2}{y^2} = \frac{b(1 - x)}{a(1 - y)}$$

$$\frac{x}{y} = \sqrt{\frac{b(1 - x)}{a(1 - y)}}$$

In the case of weak electrolytes in moderate concentration, x and y are both small as compared with 1, so the expressions $1 - x$ and $1 - y$ may each be considered as practically equal to 1, and the equation simplifies to

$$\frac{x}{y} = \sqrt{\frac{b}{a}}$$

Thus the ratio of extents of dissociation is the inverse ratio of the square roots of the concentrations. In the case of ammonium hydroxide, at the concentrations entering into the calculations previously made, this relation holds, so that the ratio of the extent of dissociation in 0.5 M solution to that in 0.1 M solution is

$$\sqrt{\frac{0.1}{0.5}} = \sqrt{\frac{1}{5}} = \frac{1}{2.236}$$

$$\frac{1}{2.236} \times 1.34 = 0.60$$

As the extent of dissociation becomes great enough so that it is no longer very small as compared with 1, a change in concentration of the solution produces a smaller change in the extent of dissociation of the compound. The limiting values for x and y are 1, and as this limit is approached the change in extent of dissociation of the compound with dilution approaches zero. This is the case of strong electrolytes and of weak electrolytes when very dilute.

The remarkable effect of a strong electrolyte on the dissociation of a weak electrolyte, with which it has an ion in common, has already been noted. The discussion just completed applies to the ionization of a compound in solution by itself. When another compound is present to supply a common ion, the situation becomes different and the above generalizations no longer apply.

Problem. What is the extent of dissociation of ammonium hydroxide in 0.1 M solution containing ammonium chloride (0.2 M, completely ionized)? ($K_{NH_4OH} = 0.0_418$).

Let x = extent of dissociation of the NH_4OH

Then $[NH_4^+] = 0.2 \text{ (from } NH_4Cl) + 0.1x \text{ (from } NH_4OH)$

$[OH^-] = 0.1x$

$[NH_4OH] = 0.1(1 - x)$

$$\frac{(0.2 + 0.1x)(0.1x)}{0.1(1 - x)} = 0.0_418$$

Since $0.2 + 0.1x$ = approximately 0.2

and $1 - x$ = approximately 1

the equation becomes

$$\frac{(0.2)(0.1x)}{0.1} = 0.0_418$$

$$0.2x = 0.0_418$$

$$x = 0.0_49$$

On comparing this result with the one obtained earlier (p. 36) for the ionization of 0.1 *M* NH_4OH in the presence of 0.5 *M* NH_4Cl, it will be seen that the extent of dissociation of the NH_4OH varies inversely as the concentration of the NH_4Cl (0.0_49 in 0.2 *M* NH_4Cl, as compared with 0.0_436 in 0.5 *M* NH_4Cl solution). Further, if one calculates the extent of dissociation of 0.5 *M* NH_4OH in the presence of 0.2 *M* NH_4Cl, essentially the same value will be obtained as above for 0.1 *M* NH_4OH. Therefore it appears that the extent of dissociation of ammonium hydroxide depends upon the concentration of the ammonium chloride, but is independent of the concentration of the ammonium hydroxide. Under such conditions the concentration of hydroxyl ion varies directly with the total concentration of ammonium hydroxide in the solution and inversely as the concentration of the ammonium chloride. On diluting a solution containing 0.5 *M* ammonium chloride and 0.1 *M* ammonium hydroxide with an equal volume of water, the concentration of the ammonium chloride is reduced to half what it was, so the extent of dissociation of the ammonium hydroxide is doubled; but the concentration of the ammonium hydroxide is reduced to half what it was, so the concentration of hydroxyl ion (derived from half the concentration of ammonium hydroxide and double the extent of dissociation) remains the same as before.

The effect of dilution on the extent of dissociation of an electrolyte in pure aqueous solution is intimately connected with the electrical conductance of the solution. In order to make the connection more obvious it is convenient to refer to the molar conductance of the solution. The fact that a solution will conduct electricity is explained by the presence of ions which move toward the electrodes under the influence of the forces of electrical attraction. The conductance of a particular solution will depend upon the valences of the ions, the number of ions present in given volume, and the mobilities of the ions (or readiness with which the ions pass through the solution). The effectiveness of a conductor is commonly stated in terms of the specific conductance of the substance, i.e., the conductance of a cube of 1 centimeter edge of the substance. The specific conductance

of a solution is the conductance obtained when measured with parallel electrodes each 1 square centimeter in area and 1 centimeter apart. The *molar conductance* of a solution is the specific conductance multiplied by the volume in cc. necessary to contain 1 mole of the solute. The more dilute the solution the larger the volume necessary to contain 1 mole. On comparing molar conductances for two different concentrations of the same electrolyte, two of the three factors of conductance mentioned above may be considered to cancel out; namely valences and mobilities of the ions. This leaves only the number of ions in the two solutions as a variable. Since the number of ions derived from 1 mole of the compound depends directly upon the extent of dissociation of the compound, the molar conductance should vary directly with the extent of dissociation. The ratio of molar conductances for two concentrations of an electrolyte should be equal to the ratio of extents of dissociation.

This makes it possible to use conductance measurements as a means of calculating the extent of dissociation of a compound in a particular solution. The principle involved is obvious in the following procedure. Determine the molar conductance of the given solution. Then dilute the solution a definite amount and determine the molar conductance again. It will be found to have increased. Continue diluting and determining the molar conductance until the latter approaches a constant value. This state will be reached when the compound is dissociated to such an extent that further dilution causes only slight increase in the extent of dissociation. Practically, it is difficult to make accurate conductance measurements in very dilute solutions so the maximum molar conductance is calculated rather than measured directly. Since the maximum molar conductance is the limit reached when the material is completely ionized, the ratio of molar conductance for a particular concentration of electrolyte to maximum molar conductance will be the ratio of the extent of dissociation at the given concentration to complete dissociation, which will be numerically equal to the actual extent of dissociation at the given concentration.

It has been possible to divide the molar conductance of a compound into the individual conductances of the two ions, by studying two series of compounds, one containing the positive ion with different negative ions, the other containing the negative ion with different positive ions. These values at maximum molar conductance of the compound become the molar conductances of the ions. The molar conductance of an ion divided by the valence of the ion gives the equivalent conductance of the ion. These equivalent conductances have been assembled into tables so that now it is only necessary to determine the molar conductance of the compound in a particular solution, and divide this by the sum of the molar conductances of the ions as calculated from the equivalent conductances in the tables, in order to find the extent of dissociation of the compound in the given solution.

In leaving this topic it may be worth while to emphasize the fact that the various methods of measuring extent of dissociation of electrolytes are based on assumptions that are justified by experimental confirmation in the case of weak electrolytes but not in the case of strong electrolytes. With strong electrolytes the magnetic effects of the large number of charged particles in the solution affect the freedom with which the ions move, so the extent of dissociation calculated by the above method is too low. For most purposes it may be assumed that a strong electrolyte is completely ionized in the ordinary solution.

§20. **Saturated Solutions.** — It always seems, at first thought, as if solubility were such a simple and definite thing that a solubility table should be easy to construct as well as extremely useful in predicting and understanding separations in analytical chemistry. It is true that the solubility of a solute in an inert solvent, at definite temperature and pressure, should be perfectly definite and capable of determination within the limits of accuracy of the particular measurements involved. But water itself is hardly to be considered as an inert solvent, and one is seldom if ever concerned with a pure solvent in ordinary analytical operations. The presence of other solutes may affect enormously the actual solubility of the given compound. Thus alcohol may lower the solubility of lead chloride to such an extent that precipitation of lead in this form is fairly complete, while hydrochloric acid may increase the solubility of lead chromate so much that this method of precipitating lead becomes worthless.

It is evident that a really useful solubility table should cover the solubility of each compound in the presence of each of the other common solutes in ordinary ranges of concentration and temperature, with additional notes on special cases when the effect of two or more solutes together cannot be figured from the effect of the solutes separately. The difficulty, of course, is that there is no such table nor is the information available in the literature of chemistry from which such a table could be constructed. It is true that much work has been done that would fit into such a table, but it is entirely too limited in scope and fragmentary in character to serve as the complete foundation of analytical chemistry. Incomplete as it is the tabulation of such information would fill a sizeable book, as may be seen from glancing into the dictionaries of solubility by Comey and Hahn and by Seidell.

In the attempt to erect a few guide posts in the field of solubility, it is useful to distinguish between physical and chemical solubility. *Physical solubility* is the solubility of the compound in the pure solvent. *Chemical solubility* is the solubility of the compound due to chemical reaction. In typical cases this is a very useful distinction. Thus, the fact that lead chloride is less soluble in a mixture of alcohol and water than it is in water may be considered as due to a change in the solvent such that the compound

is less soluble physically. The increased solubility of lead chromate when dilute hydrochloric acid is compared with water is due to chemical reaction between the lead chromate and the hydrochloric acid. Frequently such reactions have been studied in sufficient detail so that it is possible to calculate the extent of such chemical solubility. If the reaction is an irreversible one the compound will have indefinite chemical solubility; if it is reversible, there will be a definite relation between chemical solubility, and the concentration of the reagent. In many cases, however, there is serious difficulty in distinguishing between physical and chemical solubility. There are no specific tests that can be applied to identify either one in the uncertain cases, so the finer distinction of the two becomes largely a matter of definition.

Since the solubility of a compound is so indefinite, it becomes difficult to state in simple terms just what is meant by a saturated solution, and yet this is the limiting state which is of great importance in analytical chemistry since it indicates the completeness with which a compound may be precipitated and the extent to which it may be dissolved. The best practical definition of a saturated solution is the following: a *saturated solution* is one whose concentration does not change when the solution is brought into contact with more of the solute. This definition distinguishes a saturated solution from an unsaturated one, whose concentration would increase as more of the solute dissolves, and from a supersaturated one, whose concentration would decrease as the excess beyond saturation separates from solution.

In studying saturated aqueous solutions of electrolytes the attempt is commonly made to find numerical relations that will be characteristic of the individual compounds. It is obvious that this cannot be the solubility, since the latter varies widely according to the other materials present in the solution. Some help is obtained by applying the notion that the total solubility of the compound is made up of two components, one the physical solubility, the other the chemical solubility. Thus, it might be considered that the molecular material has a characteristic physical solubility dependent upon the nature of the material and of the solvent; and that the ions are present due to chemical reaction so their concentrations will depend upon the extent to which ionization takes place at definite concentration of the molecular material. Other solutes in the solution may affect the physical solubility of the compound in so far as they modify the physical character of the solvent, and they may affect the chemical solubility of the compound in so far as they aid or interfere with the process of ionization.

The earliest assumption as to the effect of other electrolytes on the physical solubility of a slightly soluble compound in water was that it is negligible, that the different molecular species possess independent solubility. This simplified the treatment of the problem very much, for, if that were

true, the variations in solubility would all be variations in chemical solubility. To the extent to which chemical reactions occur with the molecules or ions of the compound these should be capable of study and measurement, and their effect on chemical solubility determined.

The simplest case to consider is that of a saturated aqueous solution containing only the one compound as solute. The total solubility is definite for fixed conditions of temperature and pressure. Then if the physical solubility is constant the chemical solubility must also be definite. This might have been predicted from the concept of ionization as a reversible reaction. If the reaction has a definite equilibrium constant and the concentration of molecular material has a definite numerical value, the product of concentrations of the ions must also have a definite numerical value, namely, the ionization constant multiplied by the concentration of molecular material. In the case of a solution containing only the one compound and its ions as solute there will be a definite extent of dissociation characteristic of the concentration of the solution and therefore the concentration of ionized material (the chemical solubility) should have a definite numerical value.

One of the interesting tests for the accuracy of this view lies in the application of the law of mass action, in the form of the common ion effect, to such a system. The effect of common ion is to repress the ionization of a compound, thus decreasing its chemical solubility. If the solution was saturated with respect to the compound before the reagent was added that supplied the common ion, the decrease in chemical solubility should result in precipitation of the compound, the amount of precipitation being equal to the decrease in chemical solubility.

Experimentally it is easy to find many cases that are explained qualitatively on this basis. Thus, if a saturated solution of lead chloride is treated with hydrochloric acid a precipitate of lead chloride forms. The decrease in solubility might be considered to be due to repression of ionization of the lead chloride. Many such cases are available for individual study. The fact that in these cases a decrease in solubility is observed makes it appear that there is considerable truth in the view suggested. According to this view the product of the concentrations of the ions of the compound should be characteristic of such a solution so long as the solution remains saturated with respect to the compound.

The readiness with which this view offered an explanation for the decrease in solubility of a compound brought about by excess of the precipitating agent led to the wide acceptance of the idea in analytical chemistry. This constant, characteristic of the chemical solubility of a compound, was given the name *Solubility Product.*

§21. The Solubility Product of a compound is the product of the molar concentrations of the ions in a saturated solution of the compound in

water.[1] If the compound is slightly dissociated the total solubility will consist largely of physical solubility and only slightly of chemical solubility. If the compound is largely dissociated the situation is reversed, and under such conditions only a slight error will be introduced by saying that the total solubility is equal to the chemical solubility. It is on the basis of this assumption that solubility products are calculated from solubility data and values obtained for a "Solubility Product Table."

Problem. The solubility of silver chloride is 1.5 mg. per liter. Calculate its solubility product. The molecular weight of silver chloride is 143.4.

$$0.0015 \div 143.4 = 0.0_4105$$

This is the molar concentration of a saturated aqueous solution of silver chloride. Assuming that the silver chloride is almost completely ionized the concentrations of silver ion and of chloride ion will each be 0.0_4105 *M*. The product of the concentrations of the two ions will be $(0.0_4105)^2$, or 0.0_911, the solubility product of silver chloride.

(In Chemistry it has become customary to use *L* as the symbol for solubility product, this being the first letter of the German word, Löslichkeitsproduct.)

Using the solubility product it is possible to calculate the repression of solubility to be expected from a known excess of precipitating agent.

Problem. Calculate the concentration of silver ion in a saturated solution of silver chloride containing sufficient hydrochloric acid so that the concentration of chloride ion is 0.01 *M*, if $L_{AgCl} = 0.0_911$.

$$[Ag^+] = \frac{L_{AgCl}}{[Cl^-]} = \frac{0.0_911}{0.01} = 0.0_711$$

= molar concentration of silver ion in the given solution.

By comparison with the concentration of silver ion in a saturated aqueous solution of silver chloride, this value is 0.00105 as much as the latter. It might be considered that the solubility of silver chloride has thus been reduced to 0.0_711. As a matter of fact such an assumption is frequently made, but it is not justified on either theoretical or practical grounds. First, the total solubility is made up of both physical and chemical solubility. While the assumption is undoubtedly justified that in a saturated aqueous solution the physical solubility is negligible as compared with chemical solubility, it is not at all certain that this is still the case when the latter has been reduced to 0.001 what it was. If the material was 99% ionized in the first case its physical solubility under the new conditions is ten times the chemical solubility, if it was 99.9% ionized in the first case the two solubilities are now equal and the chemical solubility

[1] The definition given here for the solubility product of a compound applies only to the simplest type of salt; namely, one which yields only 2 ions from each molecule that dissociates. In its more general form the solubility product formulation requires that the concentration of each ion be raised to a power equal to the number of such ions derived from 1 molecule of the compound (see §22, p. 48).

is only half the total solubility. Practically, it is interesting to note that the minimum solubility of silver chloride in the presence of excess of chloride ion is 0.03 mg. per liter, 0.02 that in pure water.

Another important fact to consider, in using excess of precipitating agent to render the compound less soluble, is that other chemical reactions frequently take place which more than offset the reduction of solubility accomplished by repression of ionization. To the extent to which the reagent may react with either the molecules or the ions of the compound to form new chemical substances the solubility of the compound will increase. Frequently the precipitate that first forms redissolves as excess of precipitating agent is added. Thus when lead nitrate solution is treated with sodium hydroxide, a white precipitate of lead hydroxide forms, but as more of the reagent is added the precipitate dissolves giving a clear solution. The cases in which this occurs to an obvious extent are well known and dealt with in classes under such headings as "amphoteric hydroxides," "complex ammonia ions," etc. This condition is more widespread, however, than is commonly realized because in the less obvious cases it is more difficult to recognize unless quantitative experiments are employed. Thus in the ordinary qualitative test it is not obvious that silver chloride is appreciably soluble in hydrochloric acid. The following quantitative data present a different story:

TABLE 7

SOLUBILITY OF AgCl IN HCl

M-concn. of HCl	0.00	0.65	1.30	2.57	5.51
M-solv. of AgCl	0.0_4105	0.0_432	0.0_313	0.0_361	0.0_251

On the basis of these facts it now becomes necessary to distinguish two kinds of chemical solubility, (1) that due to ionization and the presence of ions of the compound in solution, (2) that due to other chemical reactions resulting in the formation of new chemical substances from either the ions or the molecules of the compound. If the precipitating agent is capable of reaction with the compound in the second way, it may affect the solubility of the compound in two ways, (*a*) decreasing the solubility by repression of ionization, (*b*) increasing the solubility by secondary reaction. The total effect on solubility will be the sum of these individual effects. Since chemical solubility of the first sort has finite value while that of the second sort will usually be very low in a saturated solution of the compound in pure water, it is to be expected that the addition of common ion will, at the start, decrease solubility of the first sort to a greater extent than it increases solubility of the second sort. But as the concentration of the reagent increases, the first effect becomes less and less while the second effect becomes steadily greater. On this basis the normal solubility curve,

starting with the value for the compound in pure water, shows a decrease to some minimum value as the concentration of a reagent supplying common ion increases. If no secondary reaction takes place the minimum value approaches the physical solubility of the compound as a limit. If secondary reaction takes place the total solubility increases again after the minimum is reached and may become many times that of the solubility of the compound in pure water. It may even happen that the increase in solubility by secondary reaction offsets the decrease in solubility by repression of ionization from the very start, in which case the minimum solubility is that of the compound in pure water and the value rises from that point on.

Probably this will all be more obvious by reference to a hypothetical case. Let us suppose a compound is available for study which is 98% ionized in a saturated solution in water. Let us suppose, further, (1) that the decrease in ionization will vary directly as the concentration of the common ion, and (2) that the increase in solubility will vary directly as the concentration of common ion. Then we may distinguish three solubilities; solubility I, or physical solubility, solubility II or chemical solubility of the first sort, and solubility III, or chemical solubility of the second sort. The sum of the three will be the total solubility. For the sake of illustration it may be assumed, further, that solubilities I and III are equal in the pure water solution. Numbers to represent relative changes in the three may be compared with the per cents in the saturated solution in pure water. Thus in pure water, I = 1, II = 98, III = 1, total solubility = 100

TABLE 8

Opposing Solubility Effects

$\frac{\text{Concn. of common ion}}{\text{Concn. of ion in sat. aq. soln.}}$	Soly. I	Soly. II	Soly. III	Total Soly.
1	1	98	1	100
2	1	49.0	2	52.0
5	1	19.6	5	25.6
10	1	9.8	10	20.8
20	1	4.9	20	25.9
100	1	0.98	100	101.98

It will be realized, of course, that the concentration of reagent necessary to produce one hundred fold increase in concentration of the given ion will depend on the solubility of the compound in pure water. In the case of silver chloride, whose solubility is 0.0_4105 moles per liter it would be necessary to make the solution only 0.00105 M with respect to chloride ion in order to accomplish this. In such a case, to derive any benefit from the common ion effect it is necessary to keep the concentration of chloride ion

so low that the effect of secondary reaction will less than offset the repression of ionization. In the data given above for the solubility of silver chloride in hydrochloric acid it is seen that the total solubility in 0.65 *M* hydrochloric acid is three times that in pure water.

In the material of the last few pages it should be noted that two very definite assumptions were made, (1) that physical solubility, as defined above, is unaffected by the presence of other electrolytes, (2) that ionization, under such conditions, is a perfectly reversible reaction and thus subject to the law of mass action. It is entirely possible that neither of these is justified. As a matter of fact it was early recognized that the decrease in solubility of a salt by addition of one of its ions sometimes left less of the salt in solution than the calculated concentration of molecular material in the saturated solution in pure water. This was interpreted as overthrowing the assumption that the concentration of molecular material in the solution is constant. Actually, the methods used to determine extent of dissociation were at fault and the concentration of molecular material was really less than calculated. Aside from this difficulty, it is only to be expected that with high concentrations of other electrolytes in the solution the physical character of the solvent may change appreciably, thus increasing or decreasing the physical solubility of the compound and even modifying the extent of ionization as well. This makes the problem so complex that it can hardly be solved. For the present it is simpler to look for useful generalizations on the basis of the above assumptions, than it is to attempt to include the possibilities just suggested.

The solubility product concept is a useful tool for further chemical study, and in analytical chemistry it offers direct information as to the extent to which various separations may be carried out providing the conditions are properly controlled and there are no interfering secondary reactions. That it cannot be trusted implicitly may be seen by trying the experiment of adding concentrated lead nitrate solution to a saturated solution of lead chloride. Note the absence of precipitation of lead chloride, though one might look for it on the basis of increase in concentration of the lead ion, as well as the readiness with which precipitation occurs when hydrochloric acid is added to some of the lead chloride solution.

§22. Electrolytes Dissociating into more than Two Ions. — The examples used thus far in discussing quantitative relations in ionization are all cases in which two ions are derived from one molecule. When more than two ions are derived from one molecule the same principles are involved as before though the situation may be more complex in certain details. The two reactions involved in such a case are, $A_mB_n \rightleftarrows mA + nB$, the ionization constant

$$K = \frac{[A]^m \times [B]^n}{[A_mB_n]}$$

and the solubility product $L = [A]^m \times [B]^n$ in a saturated solution of the compound.

One of the complications in this case is the fact that the material may ionize in steps. Thus it is well known that sulfuric acid undergoes primary ionization into hydrogen ion and acid sulfate ion, ($H_2SO_4 \rightleftarrows H^+ + HSO_4^-$) and secondary ionization into hydrogen ion and sulfate ion, ($HSO_4^- \rightleftarrows H^+ + SO_4^{--}$). In such a case there is no direct way to determine the ionization constant for the compound as a whole. Indirect methods, however, have frequently made it possible to estimate the ionization constants for the two reactions separately, and from those the dissociation constant of the compound is readily obtained by multiplying the two together. In such cases the secondary dissociation is always found to be less than the primary dissociation, but there is no regularity as to the extent of such decrease. Thus chromic acid and sulfuric acid are both considered strong acids so far as primary dissociation is concerned, but the ionization constant of acid sulfate ion (HSO_4^-) is 0.03, while that of acid chromate ion ($HCrO_4^-$) is 0.0_66.

The effect of common ion in repressing the ionization of an electrolyte of this type will vary as a higher power of the concentration of the ion. Thus in the use of hydrochloric acid to repress the ionization of hydrogen sulfide, the effectiveness of the hydrochloric acid varies as the square of the concentration of the hydrogen ion. To increase the concentration of hydrogen ion tenfold means to decrease the concentration of sulfide ion a hundred fold. This leads to an interesting situation so far as dilution is concerned. If a solution of hydrogen sulfide containing 0.5 *M* hydrochloric acid is diluted with an equal volume of water the concentration of hydrogen ion is lowered by one-half, so the extent of dissociation of the hydrogen sulfide will be four times what it was; but the concentration of hydrogen sulfide was lowered by one-half at the same time, so now the concentration of sulfide ion will become double what it was before diluting.

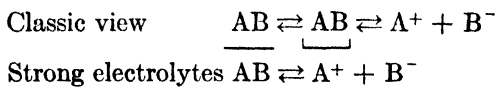
APPLICATIONS OF CHEMICAL THEORY IN QUALITATIVE ANALYSIS

§23. Mechanism of Precipitation and Solution. — Since the main tool of analytical chemistry is separation by precipitation processes, the chief interest of the analytical chemist is in the way in which precipitates are formed or kept from forming, and the way in which precipitates are dissolved or kept from dissolving.

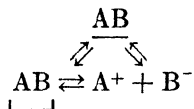
The classic view as to the mechanism of the two processes proposed the picture of a saturated solution as a system in which the precipitate is dissolving to form molecules and the molecules are separating at the same rate as a precipitate, while in solution the molecules are dissociating to form ions and the ions are combining at the same rate to form molecules. If these conditions exist and a reagent is added that will react with either of the ions, this will disturb the equilibrium in solution, causing more ionization, thus lowering the concentration of molecular material and permitting more of the solid to dissolve. On the other hand, if the solution is unsaturated with respect to a given compound and reagents are added that increase the concentrations of the ions, these will combine to form more of the molecular material and if the quantity thus formed exceeds that characteristic of a saturated solution, precipitation will take place.

Modern work on the strong electrolytes has discredited this picture of the mechanism of precipitation and dissolving of precipitates, saying that these compounds are so highly dissociated that the concentration of molecular material is negligible, that it is unnecessary to assume the formation of molecular material as an intermediate stage, and that the ions may combine to form precipitates directly and the precipitate may dissolve to form ions directly. A comparison of the two points of view may be found in the following equations:

$$\text{Classic view} \qquad \underline{\mathrm{AB}} \rightleftarrows \underbrace{\mathrm{AB}} \rightleftarrows \mathrm{A^+ + B^-}$$

$$\text{Strong electrolytes} \quad \underline{\mathrm{AB}} \rightleftarrows \mathrm{A^+ + B^-}$$

There are two difficulties with the whole-hearted acceptance of the second picture of the mechanism of chemical reactions. First, there are reactions which are very awkward to explain on that basis. Consider, for instance, the dissolving of silver chloride in hydrochloric acid. The product formed is argenti-chloride ion, $AgCl_3^{--}$. This may be considered as formed either through the combining of chloride ion with silver ion ($Ag^+ + 3\ Cl^- \rightarrow AgCl_3^{--}$) or through the combining of chloride ion with molecular silver chloride ($AgCl + 2\ Cl^- \rightarrow AgCl_3^{--}$). It is difficult to understand why the former reaction only takes place to an appreciable extent when the concentration of silver ion has been reduced to 0.0_41 what it is in a saturated solution of silver chloride in water. But it is fairly easy to see why, if the concentration of molecular silver chloride is very low, the latter reaction only takes place to an appreciable extent when the concentration of chloride ion is fairly high. To account for such reactions it is desirable to include molecular material as a possible reagent in the aqueous solution. This may be done without disregarding the argument concerning strong electrolytes by writing the equation: $\underbrace{\mathrm{AB}} \rightleftarrows \underline{\mathrm{AB}} \rightleftarrows \mathrm{A^+ + B^-}$. Second, it is desirable to have a general picture that will be equally useful for the con-

sideration of all electrolytes, whether strong or weak. The picture given at first for the strong electrolytes is obviously at fault so far as the weak electrolytes are concerned. The modification proposed of adding molecular material as an independent reagent makes it possible to consider all cases, though it gives a curious picture as to what is meant by the extent of ionization of a compound in solution. It represents the molecules and ions as two independent forms in which the material may exist in solution. But, even though they are independent, the fact that a reversible system is shown in which the molecules may be changed to ions and the ions changed to molecules through the precipitate, makes it possible for the phrase 'extent of ionization' to have its original meaning, namely the fraction of the material in solution which is in the ionic form. It is entirely feasible to speak of ionization constants, repression of ionization etc., from this point of view. However, since it is much simpler to consider that ionization is a directly reversible reaction it is better to modify the picture once more and show how all cases can be handled in a direct manner. Thus:

$$\begin{array}{ccc} & \underline{AB} & \\ \swarrow\!\!\nearrow & & \searrow\!\!\nwarrow \\ \underbrace{AB} & \rightleftarrows & A^+ + B^- \end{array}$$

This presents a picture that is consistent for both strong and weak electrolytes. In the case of the weak electrolyte the concentrations of ions may be so low as to be negligible, in strong electrolytes the concentration of molecular material may be equally negligible, but for the occasional case where it simplifies the situation very much to consider the ions of the weak electrolyte and the molecules of the strong electrolyte, these are present as potential reagents. In suggesting the mechanism of a particular reaction an obvious rule may be set up, that the reaction will be considered as proceeding through the use of that material which is present in the higher concentration.

The question is frequently asked, why bother about molecules and ions in solution, why not consider that the reagent acts directly on the precipitate? The difficulty is that this destroys all possibility of correlation between the solubility of a compound in water and the readiness with which it reacts with certain reagents, a correlation that has been found very useful in actual practice. Thus it is simple to see why ammonium hydroxide is more effective as a solvent for silver chloride than for silver iodide by comparing the concentrations of silver ion in saturated aqueous solutions of the two compounds. It would be difficult to account for ammonium hydroxide not acting on solid silver iodide if it can act on solid silver chloride. Of course, from equilibrium considerations in these two cases it could be shown that accumulation of iodide ion would cause reprecipitation of the silver iodide. But in comparing the action of dilute nitric acid on copper

sulfide and on mercuric sulfide where the sulfide is oxidized to free sulfur, there is no indirect way to account for the difference of the two if the nitric acid is considered to act directly on the solid sulfide.

In the formation of precipitates, therefore, it is assumed that the reagents must supply the ions involved in sufficient amounts to more than saturate the solution with respect to the given compound. In the dissolving of precipitates it is assumed that the compound has a certain solubility in water supplying positive ions, negative ions, and undissociated molecules, and that the reagent added must react directly with one of these. Further, the reaction must establish a distinctly lower concentration of this material than that characteristic of a saturated aqueous solution if the compound is to dissolve appreciably in the reagent.

The following pages present in outline form the basis for formulating typical reactions used in qualitative analysis. They are arranged in such a way as to emphasize certain aspects of the theory of chemical reactions. If the facts involved are not entirely clear they may be obtained by consulting Parts II and III of this text. These reactions may also be used for either class or laboratory experiments.

I. The simple factors in precipitation of salts and dissolving of salts

A. Precipitation of salts

1. The reagent must supply the necessary ions.
2. The ions must be supplied in sufficient concentrations to form more of the salt than is required to saturate the solution.

Reactions to illustrate the above points

a. A few drops of ammonium chloride forms a precipitate readily with silver nitrate solution but not with silver ammonia nitrate solution containing moderate amounts of free ammonium hydroxide. (The concentration of silver ion in the silver ammonia nitrate solution is much lower than in the silver nitrate solution.)

b. Dilute hydrochloric acid produces a precipitate of lead chloride when added to 0.1 *M* lead nitrate, but not when added to 0.007 *M* lead nitrate. (The minimum solubility of lead chloride in hydrochloric acid solutions is approximately 0.007 moles per liter.)

c. Silver nitrate forms a dark red precipitate with potassium chromate, and a white precipitate with ammonium chloride. But on adding a small amount of silver nitrate to a solution containing excess of both potassium chromate and ammonium chloride, only the white precipitate is obtained. (Sil-

ver chloride is less soluble than silver chromate and precipitates readily, so the concentration of silver ion is kept too low for precipitation of silver chromate.)

B. Dissolving of salts

1. Reagent may interact with the positive ion from the salt.
2. Reagent may interact with the negative ion from the salt.
3. Reagent may interact with the molecular salt.

Reactions to illustrate the above points

a. Silver chloride dissolves fairly readily in ammonium hydroxide. (Molecular ammonia combines with silver ion to form silver-ammonia ion.)
b. Lead hydroxide dissolves in nitric acid. (Hydrogen ion combines with hydroxyl ion to form water.)
c. Silver chloride dissolves appreciably in concentrated hydrochloric acid. (Chloride ion combines with molecular silver chloride to form silver-chloride ion, $AgCl_3^{--}$.)

II. Characteristics of metal-ammonia compounds and of amphoteric hydroxides

A. Metal-ammonia compounds

1. These are typical strong electrolytes, dissociating practically completely into metal-ammonia ion as positive ion and acid radical as negative ion.
2. The metal-ammonia ion dissociates only slightly into metallic ion and molecular ammonia.
3. Metal-ammonia ion may be decomposed by reagents which combine with either the ammonia or the metallic ion.

Reactions to illustrate the above points

a. Ammonium hydroxide is a poor conductor of electricity, but if silver chloride is dissolved in it the resulting solution is a good conductor. (The concentrations of silver-ammonia ion and chloride ion resulting from the reaction are relatively high as compared with the concentrations of ammonium ion and hydroxyl ion in the ammonium hydroxide.)
b. A solution of silver-ammonia nitrate containing excess of ammonium hydroxide fails to form a precipitate of silver chloride on treatment with a few drops of ammonium chloride. (Silver-ammonia ion is slightly enough ionized so that excess of ammonia lowers the concentration of silver ion to

a sufficient extent to prevent the precipitation of the silver chloride.)

c. A solution of copper-ammonia nitrate — prepared by adding just sufficient ammonium hydroxide to a solution of copper nitrate to redissolve the precipitate of copper hydroxide which is first obtained — forms a precipitate of copper hydroxide on nearly neutralizing with nitric acid. (Hydrogen ion combines with the ammonia, causing further dissociation of the cupric-ammonia ion until the concentration of cupric ion becomes high enough to bring about precipitation of copper hydroxide in the alkaline solution.)

B. Amphoteric hydroxides

1. These compounds are weak bases, being neutralized by strong acids with accumulation of metallic radical as positive ion in the solution.
2. These compounds are weak acids, being neutralized by strong bases with accumulation of acid radical as negative ion in the solution.
3. Starting with the ordinary acid solution of a metal whose hydroxide is amphoteric, the addition of a strong base produces first the hydroxide of the metal and then a clear solution containing the metal chiefly in the form of the anion of the amphoteric acid.
4. Starting with the ordinary basic solution of a metal whose hydroxide is amphoteric, the addition of a strong acid produces first the amphoteric acid (hydroxide of the metal) and then a clear solution containing the metal chiefly in the form of the simple positive metallic ion.

Reactions to illustrate the above points

a. Lead hydroxide dissolves in nitric acid. (Hydrogen ion combines with hydroxyl ion to form water.)

b. Lead hydroxide — plumbous acid — dissolves in sodium hydroxide. (Hydroxyl ion combines with hydrogen ion from the plumbous acid to form water.)

c. Lead nitrate on treatment with successive portions of sodium hydroxide first forms a precipitate of lead hydroxide which then dissolves with accumulation of plumbite ion in the solution.

d. Sodium plumbite on treatment with successive portions of nitric acid first forms a precipitate of plumbous acid — lead hydroxide — which then dissolves with accumulation of lead ion in the solution.

III. The variety of reactions by which ions may be supplied by reagents

A. Primary dissociation

1. On adding hydrochloric acid to a solution of silver nitrate a precipitate of silver chloride is formed. (The silver and chloride ions necessary for this reaction are obtained by the direct dissociation of the reagents.)
2. On adding nitric acid to a solution of sodium plumbite a precipitate of plumbous acid is formed. (Nitric acid dissociates directly into hydrogen ion and nitrate ion, while sodium plumbite dissociates directly into sodium ion and plumbite ion, thus supplying the ions which interact.)

B. Secondary dissociation

1. On adding potassium iodide to a solution of silver-ammonia chloride a precipitate of silver iodide is formed. (The iodide ion is supplied by direct dissociation of the potassium iodide. Silver-ammonia chloride, however, is dissociated primarily into silver-ammonia ion and chloride ion, the silver-ammonia ion being only slightly ionized into silver ion and ammonia. Thus the silver ion is derived from the secondary ionization of the silver-ammonia chloride.)
2. On adding potassium dichromate to a solution of lead chloride a precipitate of lead chromate is formed. (The lead ion is supplied by direct ionization of lead chloride. Potassium dichromate, however, is dissociated primarily into potassium ion and dichromate ion. The dichromate ion reacts with water to form acid chromate ion — $Cr_2O_7^{--} + H_2O \rightleftarrows 2\ HCrO_4^-$ — which dissociates slightly into hydrogen ion and chromate ion. Thus the chromate ion is derived from hydration and secondary ionization of the potassium dichromate.)

C. Hydrolysis

1. On adding sodium carbonate to a solution of ferric chloride a precipitate of ferric hydroxide is formed. (Ferric ion is supplied by direct ionization of the ferric chloride. Sodium carbonate, however, undergoes direct ionization into sodium ion and carbonate ion. Carbonate ion combines with hydrogen ion supplied by dissociation of the water, thus causing further dissociation of the water and accumulation of hydroxyl ion in the solution. Thus the hydroxyl ion is derived from hydrolysis of the sodium carbonate.)
2. On adding ammonium chloride to a solution of sodium aluminate a precipitate of aluminic acid — aluminum hydroxide

— is formed. (The aluminate ion is supplied by direct ionization of the sodium aluminate. Ammonium chloride, however, undergoes direct ionization into ammonium ion and chloride ion. Ammonium ion combines with hydroxyl ion supplied by dissociation of the water, thus causing further dissociation of the water and accumulation of hydrogen ion in the solution. Thus the hydrogen ion is derived from hydrolysis of the ammonium chloride.)

D. Oxidation or reduction

1. On adding bromine water to a solution containing barium chloride, hydrochloric acid and sulfurous acid, a precipitate of barium sulfate is formed. (The barium ion is supplied by direct ionization of the barium chloride. The bromine water, however, oxidizes the sulfurous acid to sulfuric acid, which is highly dissociated into hydrogen and sulfate ions. Thus the sulfate ion is derived from oxidation of the sulfurous acid.)
2. On adding stannous chloride to a solution of mercuric chloride a precipitate of mercurous chloride is formed. (The chloride ion is supplied by direct ionization of the mercuric and stannous chlorides. The stannous ion, however, reduces the mercuric ion to mercurous ion. Thus the mercurous ion is derived from reduction of the mercuric ion.)
3. On passing hydrogen sulfide into a solution of potassium dichromate a precipitate of chromic hydroxide is formed. (The hydrogen sulfide is a moderately strong reducing agent, reducing the dichromate to chromic ion. As this reaction occurs hydrogen ion is used up, thus causing further dissociation of water, with accumulation of hydroxyl ion. Thus reduction of the dichromate is responsible directly for the introduction of chromic ion and indirectly for the hydroxyl ion.)

IV. The variety of reactions by which ions may be removed by reagents

A. Formation of a slightly dissociated substance (compound or complex ion)

1. On adding sodium hydroxide to a precipitate of zinc hydroxide the precipitate dissolves. (Hydroxyl ion from the sodium hydroxide combines with hydrogen ion from the zinc hydroxide forming the molecular compound water.)
2. On adding ammonium hydroxide to a precipitate of silver chloride the precipitate dissolves. (Molecular ammonia

from the ammonium hydroxide combines with silver ion to form complex silver-ammonia ion.)

B. Formation of a slightly soluble substance (which may or may not be slightly ionized)

1. On adding potassium iodide to a precipitate of silver chloride the precipitate is converted to silver iodide. (Iodide ion from the potassium iodide combines with silver ion from the silver chloride forming the less soluble, though highly ionized, silver iodide. Through removal of silver ion the chloride ion accumulates in the solution.)
2. On adding hydrochloric acid to a precipitate of zinc sulfide the precipitate dissolves. (Hydrogen ion from the hydrochloric acid combines with sulfide ion from the zinc sulfide forming the slightly soluble, and slightly ionized, hydrogen sulfide. Through removal of sulfide ion the zinc ion accumulates in the solution.)

C. Oxidation or reduction

1. On heating copper sulfide with nitric acid the copper sulfide dissolves. (The nitric acid oxidizes sulfide ion from the copper sulfide to free sulfur, thus lowering its concentration and causing copper ion to accumulate in the solution.)
2. On heating chromic hydroxide with sodium hydroxide and hydrogen peroxide the chromic hydroxide dissolves. (Chromite ion from the chromic hydroxide is oxidized to chromate ion by the hydrogen peroxide in the presence of the sodium hydroxide, thus removing chromite ion and permitting more chromic hydroxide to dissolve.)

D. Formation of an unstable substance

1. On adding acetic acid to a precipitate of barium carbonate the precipitate dissolves. (Hydrogen ion from the acetic acid combines with carbonate ion from the barium carbonate forming the unstable, and slightly ionized, carbonic acid, thus removing carbonate ion and permitting more barium carbonate to dissolve.)

V. Comparison of cases

A. Purpose of accessory reagents

1. Reagent may prevent a reaction that would normally take place.

2. Reagent may bring about a reaction that would normally not take place.

Reactions to illustrate above points

a. Compare the action of ammonium hydroxide on two solutions of magnesium chloride one of which contains considerable ammonium chloride while the other contains none. (The ammonium chloride prevents the precipitation of magnesium hydroxide which would otherwise occur.)
b. Compare the action of hydrogen sulfide on two solutions of manganous chloride, one of which contains ammonium hydroxide while the other does not. (The ammonium hydroxide causes the precipitation of manganous sulfide which otherwise would not occur.)

B. Differences of somewhat similar reagents

1. One reagent may produce a chemical change while the other does not.
2. One reagent may prevent a chemical change while the other does not.

Reactions to illustrate the above points

a. Compare the action of acetic acid and of hydrochloric acid on zinc sulfide. (Both acids supply hydrogen ion, but the difference in extent of dissociation in the two cases means that the hydrochloric acid is an effective solvent for zinc sulfide while acetic acid is not.)
b. Compare the action of ammonium chloride and of sodium chloride on sodium aluminate. (Both chlorides are highly dissociated salts, but ammonium ion combines effectively with hydroxyl ion, raising the concentration of hydrogen ion in the solution, while sodium ion does not. Thus ammonium chloride causes precipitation of aluminum hydroxide, while sodium chloride does not.)
c. Compare the action of potassium dichromate on two solutions of barium chloride, one of which contains a moderate amount of hydrochloric acid while the other contains a corresponding concentration of acetic acid. (Both acids supply hydrogen ion, but the difference in extent of dissociation in the two cases means that the hydrochloric acid represses the ionization of acid chromate ion — $HCrO_4^-$ — sufficiently to interfere seriously with the precipitation of barium chromate, while acetic acid does not.)

d. Compare the action of hot dilute hydrochloric acid and of hot dilute nitric acid on copper sulfide. (Both acids supply high concentration of hydrogen ion, therefore both should be equally effective in removing sulfide ion if the formation of hydrogen sulfide were the only reaction involved. But nitric acid is sufficiently powerful as an oxidizing agent to oxidize sulfide ion to free sulfur. This is a more effective means for removal of sulfide ion than conversion to hydrogen sulfide. Thus copper sulfide dissolves readily in nitric acid, but with difficulty in hydrochloric acid.)

§24. Theory of Group Separations. — With the aid of the material presented in the preceding pages it will be interesting to return to a consideration of the procedures actually used in qualitative analysis. Attention has already been called to the fact that the elementary course resorts exclusively to precipitation reactions for the purpose of separating the metals considered into a number of groups. This is the first step in the analytical procedure. For this purpose a series of group reagents must be chosen and tried out experimentally. The group reagents employed in this book have already been mentioned: hydrochloric acid for Group I, hydrogen sulfide in acid solution for Group II, ammonium hydroxide in the presence of ammonium chloride for Group III, hydrogen sulfide in alkaline solution for Group IV, and ammonium carbonate for Group V. Frequent hints have been thrown out that these reagents are not as satisfactory as might be desired. On that basis one might expect to find various other sets of group reagents suggested by different workers in the field. It is true that articles appear from time to time in the chemistry journals advocating alternative reagents. An examination of a number of the standard books in the field, however, shows a surprisingly narrow range of reagents actually used. In fact, the only significant variation from the list given above is found in the frequent dropping of ammonium hydroxide as a group reagent, thus employing hydrogen sulfide in alkaline solution for the precipitation of Group III.

At first thought one might wonder whether the failure to diversify the procedure for qualitative analysis is due to inertia (laziness) on the part of the teacher or textbook writer. There are a hundred or so of reagents available in the ordinary laboratory. It would seem as if chemists with a normal amount of curiosity would try them out to see experimentally what they would do. If, from such studies, procedures were uncovered distinctly superior to the ones in common use there would certainly be a large enough group of open-minded individuals to test these and adopt them in place of the old. It is impossible to believe that no such experimentation has taken place, and that everyone has been content to continue teaching the

methods he learned as a student, in spite of their generally recognized inadequacy.

The only alternative left is to believe that there must be something in the nature of the reagents themselves or in the precipitation process that thus limits the useful ones to so small a number. It may prove instructive to consider the situation from this point of view.

Starting with the idea that the first group reagent should precipitate only three or four metals, and that each successive group reagent should precipitate only a small number of those remaining in solution, it is enlightening to check over a solubility table for the more obvious possibilities. The only acid radicals forming few enough precipitates with the metals so that they would make reasonable first group reagents are the chloride and bromide. These precipitate silver and mercury (as mercurous ion) quite satisfactorily, while the lead salts are of an intermediate degree of solubility such that precipitates form if a large amount of lead is present but not with a small amount of lead. Under certain conditions it is possible to precipitate bismuth and antimony fairly completely as basic halides (BiOCl, etc.). There is so little choice between the two reagents from the point of view of accuracy of analysis that other considerations such as availability, cost, and even stability, lead to the selection of the chloride instead of the bromide.

Next in order, so far as number of insoluble or slightly soluble salts are concerned, come sulfate, sulfite, iodide, chromate and oxalate. In all of these cases too many ions precipitate to make any of these reagents useful for Group I, but they offer possibilities for Group II and Group III reagents. Two of these, sulfate and iodide, are derived from strong acids and therefore the reagents supplying them would not be affected appreciably by either hydrogen or hydroxyl ions. In other words, these reagents may be used effectively to introduce their precipitating ions into the solution whether the solution is acid or alkaline. On the other hand, sulfite, chromate and oxalate ions combine readily with hydrogen ion to form the slightly dissociated acid-sulfite (HSO_3^-), acid-chromate ($HCrO_4^-$), and acid-oxalate ($HC_2O_4^-$) ions. Therefore the reagents used to introduce these ions must be employed in neutral or alkaline solution if it is desired to obtain reasonably high concentrations of the negative ions as precipitating agents. But many of the metals form insoluble hydroxides or basic salts in neutral or alkaline solution so it is impossible to employ reagents requiring such conditions until these metals have first been removed, otherwise the group precipitate will contain hydroxides and basic salts of these metals as well as the salts expected from the group reagent added. From this it would appear that the various groups should all be precipitated from an acid solution, thus avoiding difficulties of the sort just mentioned. Unfortunately the list of strong acids is rather limited and their precipitation reactions are not sufficiently varied to include even a majority of the com-

mon metals. The only alternative is to precipitate the first few groups from an acid solution and then complete the group separations in neutral or alkaline solution.

In this discussion it has been assumed that the precipitating ion should be added in relatively high concentration so as to take advantage of the decrease in solubility resulting from the common ion effect, thus obtaining more complete precipitation of the salts being formed. It is true, however, that if the salts are sufficiently insoluble, precipitation may take place with reasonable completeness even under relatively unfavorable conditions. In order that this may occur it is necessary that the precipitates have extremely low solubility. In re-examining the solubility data from this point of view it is found that the only salts that meet this condition are the sulfides. There are a few cases of other weak acids that form one or two precipitates in acid solution, but only in the case of the sulfides is the number great enough to form a reasonable group. The number of insoluble sulfides is fairly large, but only part of them are of sufficiently low solubility to precipitate readily in moderately acid solution. The break in solubility between the sulfides of extremely low solubility and those of the ordinary range is great enough to permit a fairly sharp separation of the two sets of metals from each other by careful adjustment of the acidity of the solution before treatment with hydrogen sulfide. The number that precipitate in acid solution still form a somewhat unwieldy group. This is improved slightly by preliminary removal of Group I with hydrochloric acid, but the use of potassium iodide or sulfuric acid as possible Group II reagents would accomplish little toward the reduction of the size of the hydrogen sulfide group, and so neither of these has come into general use.

Thus one comes to the section of the procedure in which separations must be carried out in neutral or alkaline solutions. In view of the probable precipitation of hydroxides or basic salts as the solution is neutralized, the first obvious case to consider is whether these compounds themselves may be used to form a satisfactory analytical group. The number of insoluble hydroxides, however, in the case of metals left in the filtrate from Group II, is too large to constitute a satisfactory group. The next possibility is to consider whether these hydroxides may show several distinct ranges of solubility. If such were true it might be feasible to carry out the precipitation of one or more groups by careful adjustment of the concentration of hydroxyl ion in the solution. This is attempted in the scheme employed in this book, using ammonium hydroxide as a weak base to supply low concentration of hydroxyl ion, first adding ammonium chloride to the solution to repress the ionization of the ammonium hydroxide, and avoiding any considerable excess of the reagent. Under these conditions ferric, chromic, and aluminum hydroxides precipitate readily, but cobalt, nickel, zinc, manganese, and magnesium hydroxides fail to precipitate. The separations, however, are not so satisfactory as might be expected from the

individual experiments; a fact which is commonly accounted for by saying that the first three hydroxides mentioned adsorb the others to varying extents. Experimentally it has been found that the separations can be improved considerably by careful attention to the following points: (1) use large excess of ammonium chloride, (2) use dilute ammonium hydroxide, and (3) add only a slight excess of this latter reagent.

The formation of another group by precipitation with a higher concentration of hydroxyl ion does not work out well practically for two reasons. First, the removal of ammonium ion would be a necessary first step. This could not be accomplished by merely adding hydroxyl ion to the solution, because the ammonium hydroxide thus formed would convert cobalt, nickel and zinc ions into complex metal-ammonia ions, thus interfering with the precipitation of these metals as hydroxides. It would be necessary, therefore, to remove the ammonium hydroxide thus formed by prolonged boiling before satisfactory precipitation would take place. Other methods for the removal of ammonium ion might be used in place of this one, such as evaporating the solution to dryness and gently igniting the residue ($NH_4Cl \rightarrow NH_3 + HCl$), or adding concentrated nitric acid and evaporating carefully until the residue is almost dry ($NH_4NO_3 \rightarrow N_2O + 2H_2O$). These are all somewhat tedious procedures, though they are all used in quantitative analysis and could be employed here if necessary. The second difficulty with the use of higher concentrations of hydroxyl ion to precipitate the upper range of insoluble hydroxides is concerned with the reagent itself. Ordinary sodium hydroxide contains considerable amounts of sodium carbonate. If such a reagent were used there would be precipitated insoluble carbonates of barium, strontium and calcium, as well as the hydroxides desired. Such a reagent is obviously unsatisfactory. It is rather a complex matter to prepare a solution of sodium hydroxide free from sodium carbonate and to keep it in this condition. This involves the removal of sodium carbonate already present in available sodium hydroxide and rigid protection of the final solution against contamination from carbon dioxide in the air. These difficulties are not insurmountable, but they are sufficient to suggest that it is hardly feasible to provide such a reagent for the somewhat casual use of large classes.

Thus, one comes finally to consider the other negative ions available as group reagents in alkaline solution. With the solution ammoniacal and containing high concentration of ammonium chloride, the sulfides are the only salts sufficiently insoluble to be obtained as precipitates in the case of cobalt, nickel and zinc. If this procedure is employed, manganese sulfide will precipitate at the same time. Manganese might be precipitated as hydrated manganese dioxide by the use of a proper oxidizing agent, but this offers no advantage over the inclusion of this metal in the ammonium sulfide group. Barium, strontium and calcium may be precipitated as carbonates or oxalates. Precipitation of the former is incomplete in the

presence of considerable ammonium chloride, while the oxalate precipitate might include some magnesium and manganese as well if used as the first reagent in alkaline solution. Further, the oxalates would present difficulty in analysis as a group, because of failure of the oxalic acid to be destroyed in the usual dissolving process and the resulting necessity of trying to devise separations in the presence of sufficient acid to prevent the reprecipitation of the oxalates. It is, of course, possible to remove oxalic acid by prolonged digestion with nitro-hydrochloric acid, or the separations may be carried out by the use of mixed reagents such that the barium and strontium precipitate as carbonates and only the calcium forms an oxalate. The latter procedure is not as simple as it appears, however, and so, on the basis of ease and simplicity in the further analysis of the precipitate, the alkali earth metals are usually precipitated as carbonates. If ammonium carbonate were to be used as the first reagent in the alkaline solution it would be necessary to get rid of most of the ammonium chloride first in order to obtain satisfactory precipitation of the barium, strontium and calcium carbonates. Under these conditions, however, manganese is oxidized fairly readily by atmospheric oxygen, forming the insoluble hydrated manganese dioxide, and so would precipitate to a distinct extent with the carbonates. Thus the conclusion is reached that the commonly followed scheme of group separations possesses the combined qualities of simplicity and accuracy to as great an extent as any that might be devised with the available reagents.

It is worth while in this connection to stress the fact that it has been found impossible to select a series of reagents for the purpose of group separations that can be used in haphazard fashion, making sure only that sufficient has been added to precipitate each group completely. Instead of so happy a situation, the actual case is that, in every group from the first to the last, careful attention must be paid to the conditions for precipitating the group and to the concentration of the reagent added. This is frequently not fully realized. In fact only in the precipitation of Group II are the troubles of failure to adjust conditions properly stressed sufficiently to make the student fully conscious of the empirical nature of the separations involved. Even in this group the effect of chloride ion in interfering with the precipitation of cadimum and lead sulfides is seldom if ever mentioned. In order to call attention to the general prevalence of this situation, the problem of group separations may well be considered briefly for each of the groups in turn.

§25. Group Separations in the Present Scheme of Analysis. — *Chloride ion* is used for the precipitation of Group I. The solution must be cold if lead chloride is to precipitate with even a slight degree of completeness. It must be neutral or acid if silver and lead are to be present in the form of the simple positive ions for satisfactory precipitation as chlorides. Also

the presence of moderate concentration of hydrogen ion is necessary to prevent partial precipitation of bismuth and antimony as oxychlorides in Group I. A reagent of fairly high concentration (2–5 *N*) should be used and added in a moderate excess. If the concentration of chloride ion is kept below 0.05 *N*, lead may be carried over completely into Group II, but under such conditions considerable bismuth oxychloride may precipitate in Group I unless the concentration of nitric acid is at least 2 *N*. With higher concentrations of chloride ion, partial precipitation of lead in Group I will take place if there is a moderate or large amount of lead present. Precipitation of lead chloride is made more complete as the concentration of chloride ion rises, reaching a maximum when the latter becomes slightly more than normal. Beyond this the precipitation of lead becomes less complete again due to complex-ion formation. This latter effect is obtained also in the case of bismuth, higher concentrations of chloride ion helping to prevent the precipitation of the oxychloride in Group I. In the case of silver chloride, which is much less soluble than lead chloride, the condition of minimum solubility occurs at approximately 0.01 *N* chloride ion concentration. At higher concentrations of chloride ion the solubility rises due to complex-ion formation, the effect becoming appreciable in a normal solution of chloride ion. Further, a normal solution of chloride ion interferes distinctly with the precipitation of lead and cadmium sulfides in Group II. It is impossible, therefore, to select a single concentration of chloride ion that will be best suited for the precipitation of each of the Group I ions. Out of these various considerations it appears evident that if the original solution is alkaline it must first be acidified, using nitric acid, not hydrochloric acid, for this purpose. Second, the solution should be 1–2 *N* with respect to free acid. Third, it should be cold when precipitation is completed. Fourth, in adding excess of chloride ion to obtain complete precipitation, the final concentration should not exceed 0.5 *N*. This last will leave the precipitation of lead chloride somewhat less complete than it might be made, but since precipitation of the lead is never quantitative there is no harm done in leaving just a little more in solution to be identified in Group II.

§26. Sulfide ion is the precipitating agent for Group II. Experimentally it has been found that in a 0.25 *N* hydrochloric acid solution, hydrogen sulfide will precipitate readily the sulfides of mercury, lead, bismuth, copper, cadmium, tin, antimony and arsenic (except quinquivalent arsenic), while with moderate concentrations of later group metals, precipitation takes place only very slowly or not at all. Therefore a separation of Group II from later groups should be obtained if these conditions can be maintained during the precipitation process. These conditions presuppose that the solution becomes approximately saturated with respect to hydrogen sulfide. This gas is slightly soluble in water at room temperature,

forming a 0.1 *M* solution if the gas is absorbed under atmospheric pressure. Sometimes, from samples of iron sulfide containing free iron, the gas obtained by the action of acid consists of both hydrogen and hydrogen sulfide. Under such conditions the partial pressure of the hydrogen sulfide will be less than atmospheric pressure and therefore it will not dissolve to the extent assumed above. On the other hand treatment with hydrogen sulfide in a closed precipitation flask may introduce the gas into the solution at considerably above atmospheric pressure, although commonly the gas generators are not run at more than 5% above atmospheric pressure. In such a case the solubility may exceed the figure given.

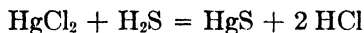
The acidity of the solution, however, is the most important factor in the situation, the hydrogen ion controlling the extent of dissociation of the hydrogen sulfide. The concentration of sulfide ion must be permitted to become high enough for the precipitation of Group II, but not for the precipitation of later group metals. In this connection it should be noted that the formula for the ionization constant of hydrogen sulfide

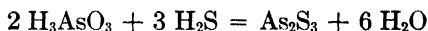
$$K_{H_2S} = \frac{[H^+]^2 \times [S^{--}]}{[H_2S]}$$

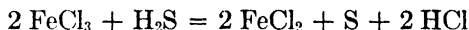
involves the square of the concentration of the hydrogen ion and only the first power of the concentration of the sulfide ion. In other words, for a given concentration of hydrogen sulfide in the solution, the concentration of sulfide ion will vary inversely as the square of the concentration of hydrogen ion. If the concentration of hydrogen ion is increased tenfold that of the sulfide ion will be decreased one hundred fold, or if the concentration of hydrogen ion is decreased tenfold that of the sulfide ion will be increased a hundred times. It is readily seen, therefore, that attention must be paid to reasonably careful adjustment of the acidity of the solution before precipitating Group II with hydrogen sulfide.

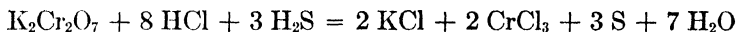
There are several difficulties involved in setting up and maintaining the desired acidity. As indicated above, the selection of the proper acidity was made experimentally. It may be defined as the concentration of hydrogen ion corresponding to a 0.25 *N* solution of hydrochloric acid. The obvious procedure to obtain this would be to neutralize the somewhat indefinite amount of free acid present in the filtrate from Group I, and then add a proper volume of hydrochloric acid of known concentration. Thus, to the neutral solution add one-nineteenth its volume of 5 *N* hydrochloric acid or one-third its volume of 1 *N* hydrochloric acid, etc. But, with various metals of Group II and later groups present, their hydroxides precipitate as the solution is neutralized, and these react with the acid then added so the actual acidity of the solution will be less than calculated. Again, if the solution contains weak acids, acetic acid, arsenious acid, etc., these will be neutralized, forming acetate and arsenite ions; then when the

hydrochloric acid is added, these ions will combine with the hydrogen ion, preventing its accumulation in the solution to the desired extent. A third source of uncertainty as to the actual concentration of hydrogen ion in the solution is found in the reactions that take place during the precipitation process. As Group II sulfides precipitate, the acidity of the solution generally increases. This may be shown by the equation for the precipitation of mercuric sulfide:

$$HgCl_2 + H_2S = HgS + 2\,HCl$$

Note, however, that this is not the case with arsenic, where the acidity decreases slightly:

$$2\,H_3AsO_3 + 3\,H_2S = As_2S_3 + 6\,H_2O$$

Further, hydrogen sulfide is a strong reducing agent, and, if the solution contains oxidizing agents, reactions may occur that will affect the acidity of the solution. Ferric salts are reduced with increase in concentration of hydrogen ion in the solution:

$$2\,FeCl_3 + H_2S = 2\,FeCl_2 + S + 2\,HCl$$

On the other hand, a dichromate or permanganate would be reduced with decrease in the acidity of the solution:

$$K_2Cr_2O_7 + 8\,HCl + 3\,H_2S = 2\,KCl + 2\,CrCl_3 + 3\,S + 7\,H_2O$$

Since cases of this last sort might result in sufficient neutralization of the solution to permit the precipitation of sulfides or basic salts of later group metals along with those of Group II, it is obvious that provision must be made to avoid such difficulties. Thus the filtrate from Group I is examined for dichromate and permanganate ions. If these are present they are reduced before attempting to adjust the acidity of the solution.

Two methods are commonly used to set up a reasonable concentration of hydrogen ion in the case where the volume of the solution is kept small (20–30 cc.). The one proposed by Stieglitz[1] uses a dilute solution of an organic dye, methyl violet (0.08 g. per liter), as an indicator whose blue green color when 2 drops of the unknown solution are added to 2 drops of the indicator solution identifies a concentration of hydrogen ion corresponding to 0.2–0.25 *N* hydrochloric acid, as distinct from 0.1 *N* and 0.33 *N* acid, the former giving a clear blue color and the latter a yellow-green. Dilute ammonium hydroxide may be added in small amounts at a time until a test portion of the solution gives the proper color with the methyl violet. The other method neutralizes the solution, as indicated above, then adds hydrochloric acid, a few drops at a time, until a slight acid re-

[1] Stieglitz, I, 214

action is shown with litmus paper. This solution is then considered as the "neutral solution" to which the measured volume of hydrochloric acid is added. If a precipitate still persists, having an appearance other than white and flocculent (BiOCl, etc.), it should be dissolved in the minimum amount of hydrochloric acid necessary. In both of these cases the extra acid formed during the precipitation process may be taken into account by diluting the filtrate from the first precipitate before testing further with hydrogen sulfide for completeness of precipitation. If the sum of the equivalent concentrations of Group II metals and of ferric iron does not exceed 0.25 *N*, the acidity will not more than double on treatment of the solution with hydrogen sulfide. On that basis, diluting the solution with an equal volume of water will be sufficient to restore an acidity that will permit ready precipitation of even small amounts of cadmium and lead. Since 20 cc. of 0.25 *N* copper chloride will contain 160 mg. of metal, and the same amount of mercuric chloride will contain 500 mg. of metal, the above procedure will be adequate for a reasonable range of concentrations of metals in the solution. (Copper and mercury have been considered here since they represent the extremes of equivalent weights of Group II metals whose precipitation as sulfides increases the acidity of the solution.)

Another method of handling this situation is that used by Noyes.[1] By working in a larger volume, more acid is required to set up a definite acidity, and under such conditions the amount of acid involved in the various effects noted above may be exceeded sufficiently by that already present to make the changes in acidity negligible in amount. Thus if the volume of the solution is 100 cc. there must be the equivalent of 5 cc. of 5 *N* hydrochloric acid present in the solution to make it 0.25 *N* with respect to the acid. At 200 cc. volume, 10 cc. of the 5 *N* acid would be required. If the quantities of the various materials in the solution are such that the maximum change produced would correspond to only 2.5 cc. of the 5 *N* acid, the range in acidity in the 100 cc. volume would be from 0.125 to 0.375 *N*; or in 200 cc., from 0.187 to 0.312 *N*. The latter is well within the necessary range, and even the former will avoid any serious trouble if reasonable care is taken in treating the solution with hydrogen sulfide. In this method all that is necessary is to neutralize the solution approximately, add 5 cc. of 5 *N* hydrochloric acid, dilute to 100 cc., treat with hydrogen sulfide until precipitation appears to be complete, filter, and test the filtrate with more hydrogen sulfide for completeness of precipitation.

The argument that first occurs to the student against working in a larger volume is that precipitation would be less complete due to the actual solubility of the compound. For most of the analytical precipitates, however, the solubility is sufficiently low so that this becomes insignificant for ordinary purposes in the volumes under consideration. As a matter of fact, decreased adsorption of soluble materials by the precipitate in the

[1] Noyes, 66.

more dilute solution probably increases the accuracy of the separations more than it is decreased by the solubility of the precipitates being formed. The only valid reason for not working in the larger volume lies in the extra time required for precipitation and filtration. Since the number of these operations is fairly large in the systematic analysis of a general unknown, it may seem desirable to decrease the time spent on these mechanical details so as to permit the examination of a greater variety of unknowns. However, this advantage is largely offset by the simplicity of the precipitation of Group II, so it is to be expected that there will be honest differences of opinion as to which of the two types of procedure is the more desirable.

There are two aspects of the precipitation of Group II that have not been included in the discussion thus far. These are, first, the effect of excess chloride ion on the precipitation of cadmium and lead sulfides, and, second, the anomalous behavior of arsenic acid, which requires a concentration of hydrochloric acid of 3 N, or higher, in order to precipitate readily as the sulfide.

The first point becomes evident in a detailed consideration of two facts noted by Stieglitz;[1] (*a*) that the precipitation of cadmium sulfide is completely prevented by the addition of 15 cc. of concentrated hydrochloric acid to 50 cc. of 0.1 M cadmium sulfate solution, and (*b*), that 1 mg. of cadmium ion in 100 cc. is readily precipitated by hydrogen sulfide in the presence of 0.25 M hydrochloric acid. The molar concentration of hydrochloric acid in the first solution is essentially 2.77, so the ratio of concentrations of hydrochloric acid in the two solutions is approximately 11:1. Let us assume, first, that the solutions are both saturated with respect to hydrogen sulfide; second, that the hydrogen sulfide has approximately the same solubility in the two cases; and, third, that the concentrations of hydrogen ion are in approximately the same ratio to each other as the molar concentrations of the acid. Then the concentration of sulfide ion in the solution of lower acidity will be essentially 132 (11^2) times that in the solution of higher acidity. Therefore it is to be expected that the ratio of concentrations of cadmium ion to each other in the two solutions will be somewhat less than 132 : 1. But 50 cc. of 0.1 M cadmium sulfate contain 562 mg. of cadmium so the ratio of the concentration of cadmium in the more concentrated solution to that in the more dilute solution will be 865 : 1, (562 mg. in 65 cc., as compared with 1 mg. in 100 cc.). Since the precipitate does not appear in the more concentrated solution, but forms readily in the dilute one, the actual ratio for equivalent effects is probably several times as great as the figure given. Since the hydrogen ion accounts for a possible difference of not more than one hundred thirty-two fold in the concentrations of cadmium ion in the two solutions, it is evident that there must still be another factor involved in the results obtained. This other factor may well be found in the reaction of chloride

[1] Stieglitz, I, 211, footnote 2, and 214, footnote 1.

ion with cadmium ion to form molecular cadmium chloride or a complex cadmium-chloride ion ($CdCl_4^{--}$), so that the ratio of concentrations of cadmium ion in the two solutions is much less than that of the molar concentrations of the cadmium salts.

This matter was examined directly by Dede and Bonin[1] who studied the effect of calcium chloride, ammonium chloride and potassium chloride, in varying amounts, on the precipitation of lead and cadmium sulfides in the presence of varying amounts of hydrochloric acid. Thus, 100 cc. of 0.001 *M* lead chloride solution (20.7 mg. of lead), with varying amounts of neutral chloride and of hydrochloric acid present, were treated at 20° with hydrogen sulfide for 15 minutes, the gas being passed in at a rate such that the bubbles could just be counted. Table 9 shows the concentrations

TABLE 9

COMPLETE PREVENTION OF PbS PPTN. (20.7 MG. Pb IN 100 CC.)

Normality of neutral chloride	Normality of HCl in presence of	
	$CaCl_2$	NH_4Cl
0 0	1 40	1.40
.2	1.25	1.27
.4	1 10	1.25
6	1 00	1.10
.8	0.90	1.00
1.0	.80	0.85
1.2	.75	.82
1.6		.60
2.0	.53	.48
2.8	.20	.15

of neutral chloride and of hydrochloric acid which completely prevented the precipitation of lead sulfide. Similar effects were noted in the case of cadmium, the conclusion being fairly obvious, for the analytical chemist, that the concentration of chloride ion as well as that of hydrogen ion needs regulating if satisfactory precipitation of Group II is to be obtained.

This chloride ion effect offers a reasonable explanation for the irregularity in the solubility product of cadmium sulfide as calculated by Bruner and Zawadzki from their analytical studies.[2] Their experimental data for cadmium sulfide in equilibrium with cadmium chloride, hydrogen sulfide, and hydrochloric acid led to a value, 7.1×10^{-28}; while for cadmium sulfide in equilibrium with cadmium sulfate, hydrogen sulfide and sulfuric acid, the value obtained was 5.1×10^{-29}. The authors referred these

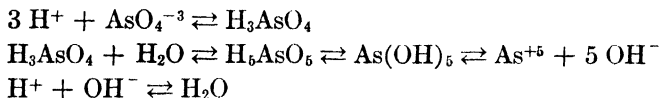
[1] Dede and Bonin, *Ber.*, **55B**, 2327 (1922).

[2] Bruner and Zawadzki, *Z. anorg. allgem. Ch.*, **65**, 135 (1909).

differences to possible variations in the solid phase, but the present suggestion offers a simpler explanation.

The behavior of arsenic acid with hydrogen sulfide is an experimental fact that must be taken into account in setting up procedures for the precipitation of Group II. Arsenic sulfide precipitates very slowly on treatment of a hot solution of arsenic acid with hydrogen sulfide in the presence of 0.25 *N* hydrochloric acid. But if the concentration of hydrochloric acid is increased considerably, the precipitate forms readily. The lower limit of acidity for satisfactory precipitation lies at 2.5–3 *N*; with slightly higher acidity less time is required to obtain complete precipitation. This situation is in marked contrast to that of the other metals of Group II, whose sulfide precipitations are interfered with more or less seriously by the concentrations of hydrochloric acid just mentioned.

The attempt is sometimes made to account for this irregularity of arsenic by referring to arsenic acid as amphoteric, calling attention to the effect of hydrogen ion on the dissociation of that type of substance. The following system is involved:

$$3\ H^+ + AsO_4^{-3} \rightleftarrows H_3AsO_4$$
$$H_3AsO_4 + H_2O \rightleftarrows H_5AsO_5 \rightleftarrows As(OH)_5 \rightleftarrows As^{+5} + 5\ OH^-$$
$$H^+ + OH^- \rightleftarrows H_2O$$

Doubling the concentration of hydrogen ion will increase the extent of dissociation of arsenic hydroxide, $As(OH)_5$. Since the latter is a weak base the effect produced will be to increase the concentration of arsenic ion (As^{+5}) approximately 32 fold (2^5). It might appear as if this effect were ample to account for the improved precipitation of the arsenic sulfide at higher acidities. Thus, at low acidity the concentration of arsenic ion is too low to enable sufficient arsenic sulfide to form to exceed the solubility of the compound, but at higher acidities the concentration of arsenic ion increases very considerably, enabling larger amounts of arsenic sulfide to form. However, with increased acidity the extent of dissociation of hydrogen sulfide decreases, the effect being just sufficient to offset the gain in concentration of arsenic ion. The formula for the solubility product of arsenic sulfide involves the square of the concentration of arsenic ion and the fifth power of the concentration of sulfide ion. If, then, increase in acidity is to favor precipitation of arsenic sulfide (assuming the reaction to be of the usual ionic type), it would appear that increasing the concentration of hydrogen ion should bring about an increase in the numerical value of the expression: $[As^{+5}]^2 \times [S^{--}]^5$.

Let $x = [As^{+5}]$ and $y = [S^{--}]$ in a particular solution containing arsenic acid, hydrogen sulfide and hydrochloric acid. $[As^{+5}]^2 \times [S^{--}]^5 = x^2y^5$. If the concentration of hydrogen ion is increased *n*-fold, the effect is to increase the concentration of arsenic ion approximately n^5-fold, and to

decrease the concentration of sulfide ion to $\frac{1}{n^2}$ what it was. Under these conditions

$$[As^{+5}]^2 \times [S^{--}]^5 = (n^5x)^2\left(\frac{y}{n^2}\right)^5 = n^{10}x^2\left(\frac{y^5}{n^{10}}\right) = x^2y^5$$

It is evident that the usual ionic considerations do not offer an explanation for the effect of hydrochloric acid on the behavior of arsenic acid with hydrogen sulfide. The only alternative is to consider that the precipitation of arsenic sulfide is not an ionic reaction.

There is experimental evidence[1] to justify the assumption that the reaction involves molecular interaction of arsenic acid and hydrogen sulfide, followed by decomposition of the resulting products. The following equations show the main reactions involved:

(1) $H_3AsO_4 + H_2S = H_3AsO_3S + H_2O$
(2) $H_3AsO_3S + H_2S = H_3AsO_2S_2 + H_2O$
(3) $H_3AsO_2S_2 + H_2S = H_3AsOS_3 + H_2O$
(4) $2\,H_3AsOS_3 = As_2S_5 + H_2S + 2\,H_2O$
(5) $H_3AsO_3S = H_3AsO_3 + S$
(6) $2\,H_3AsO_3 + 3\,H_2S = As_2S_3 + 6\,H_2O.$

Experimentally it appears that the effect of the hydrochloric acid is to increase the rate at which hydrogen sulfide reacts with the arsenic solutions and to establish conditions under which reaction 4 takes place readily; but the mechanism is still uncertain. To the extent to which reaction 5 occurs, arsenious sulfide is formed. The monothioarsenic acid is sufficiently stable, however, so that with a moderate current of hydrogen sulfide the precipitate is essentially arsenic sulfide.

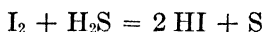
Since arsenious sulfide precipitates readily in slightly acid solution, and arsenic acid is rather easily reduced to arsenious acid, it is possible to obtain complete precipitation of Group II without resorting to the use of higher concentrations of hydrochloric acid. The reducing agent commonly used for this purpose is potassium iodide.

$$H_3AsO_4 + 2\,KI + 2\,HCl = H_3AsO_3 + I_2 + 2\,KCl + H_2O$$

This may be used in two different ways. First, excess of potassium iodide may be added and the solution boiled until the free iodine formed has been removed by volatilization. This reduces the arsenic completely to arsenious acid, which may then be precipitated with hydrogen sulfide in the usual

[1] McCay, *Am. Ch. J.*, **10**, 459 (1888), *Z. anorg. allgem. Ch.*, **29**, 36 (1901); McCay and Foster, *Z. anorg. allgem. Ch.*, **41**, 452 (1904); Foster, *J. Am. Ch. Soc.*, **38**, 52 (1916); Foerster, *Z. anorg. allgem. Ch.*, **188**, 90 (1930).

way. In the second method only a small amount (0.5–1.0 cc.) of potassium iodide solution is added, and the solution is then treated directly with hydrogen sulfide without boiling out the free iodine. The free iodine reacts with the hydrogen sulfide forming hydriodic acid, which, in turn, is oxidized again to free iodine by more of the arsenic acid present. By repetition of these steps a large amount of arsenic acid may be reduced to arsenious acid with only a small amount of potassium iodide added at the start. The equations representing these steps may be written as follows:

$$H_3AsO_4 + 2\,KI + 2\,HCl = H_3AsO_3 + I_2 + 2\,KCl + H_2O$$
$$I_2 + H_2S = 2\,HI + S$$
$$H_3AsO_4 + 2\,HI = H_3AsO_3 + I_2 + H_2O$$

Whether one prefers to reduce the arsenic acid or to carry out the precipitation of arsenic sulfide in the presence of high concentration of hydrochloric acid, it is generally agreed that the precipitation of Group II should be carried out in two stages, using hydrogen sulfide in 0.25 *N* hydrochloric acid as the first step, and leaving the special case of arsenic acid as the second step. In this way, by examining the two precipitates separately it is possible to identify the two forms of arsenic fairly well without resorting to individual tests on the original solution.

In leaving this discussion, it may be well to note that both of the above procedures introduce some additional complications into the scheme of analysis. Thus, if the solution contains a considerable amount of nitrate ion — which is usually the case in the filtrate from Group I — moderately strong oxidizing conditions are established in the solution when it is made 3 *N* with hydrochloric acid and heated. Under such conditions the arsenic sulfide formed when hydrogen sulfide is passed into the solution may redissolve before it can be filtered out. Therefore it may be necessary to carry out a preliminary operation of adding 10–15 cc. of hydrochloric acid and evaporating once or twice to approximate dryness in order to avoid this interference. On the other hand, reduction of the arsenic acid with potassium iodide leaves some iodide ion in the solution. In oxidizing ferrous ion to ferric ion at the beginning of Group III the iodide ion is oxidized to free iodine. The solution should be boiled until the iodine is all removed, before adding ammonium hydroxide for the precipitation of Group III. Otherwise there is the possibility of reaction between the iodine and the ammonium hydroxide to form the explosively unstable compound, nitrogen tri-iodide:

$$8\,NH_4OH + 6\,I_2 = 2\,NI_3 + 6\,NH_4I + 8\,H_2O$$

§27. Hydroxyl ion is the reagent suggested in the present scheme of analysis for the precipitation of Group III. There is not so great a difference in solubility, however, between hydroxides of Group III and

those of later groups as there is between the sulfides of Group II and those of later groups. Therefore, the similarity in principle of the procedures used in precipitating Groups II and III tells only part of the story. In both cases a weak electrolyte is used to supply the precipitating ion in the presence of a strong electrolyte having a common ion to keep the concentration of the reacting ion very low. Thus, hydrochloric acid is used to repress the ionization of the hydrogen sulfide in Group II and ammonium chloride is used to repress the ionization of the ammonium hydroxide in Group III. But in Group III there are certain additional factors which play a part in the accuracy of the separation from later groups.

First, ammonium hydroxide is a reagent which forms complex ions with a number of the metals, including cobalt, nickel and zinc, the three metals of Group IV whose hydroxides are least soluble. This reaction lowers the concentration of simple metallic ion in the solution thus decreasing the readiness of precipitation of compounds of these metals, including their hydroxides. By having a moderate amount of ammonium chloride in a cobalt, nickel or zinc chloride solution one may add ammonium hydroxide until the solution is alkaline and pass directly from the simple metal ion to the complex metal-ammonia ion without intermediate precipitation of the hydroxide. This same reaction takes place to a significant extent in the cold with chromium of Group III. However, the chromic-ammonia complex ion is less stable than the others just mentioned. It can be decomposed by boiling for a short time, chromic hydroxide precipitating somewhat slowly, or it may be kept from forming by having the solution hot before adding the ammonium hydroxide. From this it might appear that moderate excess of ammonium hydroxide would be desirable, aiding in the conversion of cobalt, nickel and zinc to complex ammonia ions. Experimentally, however, it is found that little is gained. Increasing the excess of ammonium hydroxide used does not decrease significantly the amount of these three metals precipitated in Group III. At the same time the higher concentration of OH^- permits further atmospheric oxidation of Mn^{++} with corresponding precipitation of manganic hydroxide, $Mn(OH)_3$, in Group III.

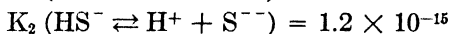
The second additional factor in the separation of Group III from later groups is found in the effectiveness of high concentrations of ammonium chloride in preventing the carrying down of cobalt, nickel and zinc in Group III. The nature of this "carrying down" is not clear. Whether the amphoteric hydroxides of chromium, aluminum and zinc supply negative ions with which other metallic ions combine to form insoluble salts (for example, $Zn(CrO_2)_2$, $Co(AlO_2)_2$, $Fe_2(ZnO_2)_3$ etc.); whether mixed hydroxides are formed ($x Fe(OH)_3 \cdot y Ni(OH)_2$, etc.); or whether the effect is one of colloidal adsorption of hydroxide, basic salt, or simple ion on the surface of the gelatinous particles of Group III hydroxides: are points that

have not been clearly settled thus far. It is a simple matter, however, to demonstrate this carrying down as an experimental fact and to study the effect of ammonium chloride on the extent to which it takes place.[1]

In passing, it should be emphasized that the separation of large amounts of Group III metals from Group IV by means of ammonium hydroxide is not a satisfactory quantitative method. With small amounts of ammonium chloride present it is a poor qualitative method; but with adequate amounts of ammonium chloride present (1–2 g. of the solid salt per 10 cc. of solution) the carrying down of Group IV metals in Group III is decreased considerably so that all of the Group IV metals can be identified in their regular places.

§28. **Sulfide ion** is the reagent used for precipitating Group IV. The essential difference between its use in Group II and in Group IV lies in the concentration in which it is employed. In Group II, hydrogen ion is introduced in moderate concentration to keep the hydrogen sulfide from ionizing to the extent to which it would in pure aqueous solution. In Group IV the solution is slightly alkaline, containing a moderate concentration of ammonium chloride. The effect of the hydroxyl ion is to neutralize the hydrogen sulfide partly, thus permitting a higher concentration of sulfide ion to accumulate than would be present in a solution of hydrogen sulfide in pure water. Because of the low values of the ionization constants for the primary and secondary ionization of hydrogen sulfide these effects are so striking that they may well be considered in some detail.

The calculations for acid solutions are made very simply by the use of the following constants:

$$K_1\ (H_2S \rightleftarrows H^+ + HS^-) = 0.9 \times 10^{-7}$$
$$K_2\ (HS^- \rightleftarrows H^+ + S^{--}) = 1.2 \times 10^{-15}$$

[1] For example: if a solution containing 5 mg. of cobalt, as $CoCl_2$, in 20 cc. of water is treated with 1 cc. of 5 *N* ammonium chloride, and then 5 *N* ammonium hydroxide is added until the solution becomes alkaline, no visible precipitate of cobalt hydroxide, or basic salt, forms. Next, to each of a series of 5 test tubes add 40 mg. of aluminum, as $AlCl_3$, and 5 mg. of cobalt, as $CoCl_2$. To the tubes 1, 2, 3, 4 and 5, in order, add 1, 2, 4, 8, and 16 cc. of 5 *N* ammonium chloride, adding sufficient water to each of the first 4 tubes to make the total volume of solution the same as in the fifth tube (23 cc.). Heat nearly to boiling, add 5 *N* ammonium hydroxide drop by drop until the odor of ammonia is just perceptible, let stand 1 to 2 minutes, filter, and wash. The precipitates from tubes 1 to 4 range in color from blue to pinkish blue, while that from number 5 is almost white, only a faint pink tinge being visible. The filtrates, evaporated to 20 cc., range from colorless to pink, showing perceptible change in shade from 2 to 5. It is evident that the cobalt is carried down to a large extent by the aluminum hydroxide under conditions which are adequate to prevent the cobalt from precipitating by itself. Further, it is interesting to note that in tube number 5, where the separation is best, the solution contains sufficient chloride ion to turn blue on heating, due to formation of a complex cobalt chloride ion, $CoCl_4^{--}$. This suggests that probably the chloride ion is involved in the decreased adsorption of cobalt by aluminum hydroxide.

A saturated aqueous solution of hydrogen sulfide is approximately 0.1 *M*. Inserting this value in the expression,

$$\frac{[H^+] \times [HS^-]}{[H_2S]} = 0.9 \times 10^{-7}$$

and noting that the further ionization of HS^- into H^+ and S^{--} will take place so slightly as not to change appreciably the concentrations of hydrogen and bisulfide ions,

$$[H^+] = [HS^-] = \sqrt{0.9 \times 10^{-8}} = 0.95 \times 10^{-4}$$

Inserting these values in the expression

$$\frac{[H^+] \times [S^{--}]}{[HS^-]} = 1.2 \times 10^{-15}$$

and solving,

$$[S^{--}] = 1.2 \times 10^{-15}$$

If, now, a 0.25 *N* hydrochloric acid solution is saturated with hydrogen sulfide, the concentration of the latter will still be approximately 0.1 *M*, but the concentration of hydrogen ion will be approximately 0.25 *M*. Using these values in the above expressions,

$$[HS^-] = \frac{0.9 \times 10^{-8}}{0.25} = 3.6 \times 10^{-8}$$

and

$$[S^{--}] = \frac{1.2 \times 10^{-15} \times 3.6 \times 10^{-8}}{0.25} = 1.7 \times 10^{-22}$$

The change in acidity from 0.95×10^{-4} *M* to 0.25 *M* lowers the concentration of sulfide ion from 1.2×10^{-15} *M* to 1.7×10^{-22} *M*, a decrease to $0.0_{6}14$ of that present in the saturated solution in pure water.

On the other hand, if 0.1 mole of hydrogen sulfide were passed into an aqueous solution of such volume that the final volume would be one liter, and containing just sufficient hydroxyl ion so that the final solution would be neutral:

$$[H^+] = [OH^-] = \sqrt{1.2 \times 10^{-14}} = 1.1 \times 10^{-7}$$

Inserting this value for $[H^+]$ in the above expressions,

$$\frac{[HS^-]}{[H_2S]} = \frac{0.9 \times 10^{-7}}{1.1 \times 10^{-7}} = 0.82,$$

and

$$\frac{[S^{--}]}{[HS^-]} = \frac{1.2 \times 10^{-15}}{1.1 \times 10^{-7}} = 1.1 \times 10^{-8}$$

The sum of the concentrations of hydrogen sulfide, bisulfide ion, and sulfide ion will be 0.1 *M*; but the concentration of sulfide ion is so low as to be a negligible part of this, therefore

$$[HS^-] = 0.045\ M, \quad \text{and} \quad [H_2S] = 0.055\ M$$

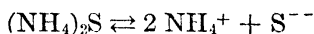
Using this value for $[HS^-]$:

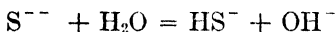
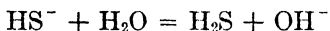
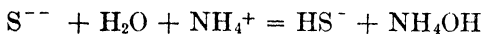
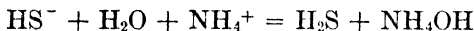
$$[S^{--}] = \frac{1.2 \times 10^{-15} \times 0.045}{1.1 \times 10^{-7}} = 4.9 \times 10^{-10}$$

Thus neutralizing a saturated aqueous solution of hydrogen sulfide increases the concentration of sulfide ion from $1.2 \times 10^{-15}\ M$, to $4.9 \times 10^{-10}\ M$, an increase of four hundred thousand fold.

It is interesting, further, to consider typical reagents that might be used to supply sulfide ion in alkaline solution. Due to the low values of the primary and secondary ionization constants, hydrolysis will take place to a considerable extent. The results of hydrolysis may be calculated for a series of solutions 0.1 *M* with respect to the reagents sodium sulfide, sodium bisulfide, ammonium sulfide, and ammonium bisulfide. The following assumptions serve as a basis for the calculations:

(1) the salts are all taken as essentially completely ionized,

$$Na_2S \rightleftarrows 2\ Na^+ + S^{--}$$
$$NaHS \rightleftarrows Na^+ + HS^-$$
$$(NH_4)_2S \rightleftarrows 2\ NH_4^+ + S^{--}$$
$$NH_4HS \rightleftarrows NH_4^+ + HS^-$$

(2) the main reactions occurring in the hydrolysis of the different solutions are

Solution	*Main Reaction*
Na_2S	$S^{--} + H_2O = HS^- + OH^-$
$NaHS$	$HS^- + H_2O = H_2S + OH^-$
$(NH_4)_2S$	$S^{--} + H_2O + NH_4^+ = HS^- + NH_4OH$
NH_4HS	$HS^- + H_2O + NH_4^+ = H_2S + NH_4OH$

(3) the numerical constants expressing the various ionic relations are

$$[H^+] \times [OH^-] = 1.2 \times 10^{-14}$$

$$\frac{[H^+] \times [S^{--}]}{[HS^-]} = 1.2 \times 10^{-15}$$

$$\frac{[H^+] \times [HS^-]}{[H_2S]} = 0.9 \times 10^{-7}$$

$$\frac{[NH_4^+] \times [OH^-]}{[NH_4OH]} = 1.8 \times 10^{-5}$$

Sodium hydroxide is assumed to be completely ionized. The results of the calculations are expressed in Table 10.

TABLE 10

RESULTS OF HYDROLYSIS OF SULFIDE SOLUTIONS

Solution	$[S^{--}]$	$[HS^-]$	$[H_2S]$	$[H^+]$	$[OH^-]$
0.1 M Na_2S	1×10^{-3}	0.099	1.3×10^{-7}	1.2×10^{-13}	0.099
.1 M NaHS	1.1×10^{-6}	.1	1.1×10^{-4}	1.1×10^{-10}	1.1×10^{-4}
.1 M $(NH_4)_2S$	1.8×10^{-7}	.099	7.4×10^{-4}	6.7×10^{-10}	1.8×10^{-6}
.1 M NH_4HS	1.2×10^{-8}	.092	0.008	7.7×10^{-9}	1.6×10^{-6}

The conditions actually employed in the precipitation of Group IV with hydrogen sulfide are intermediate between those shown in the last two cases. That is, the solution contains high concentration of ammonium chloride (3–4 M), and is made about 1 M with respect to ammonium hydroxide. This sets up a concentration of hydroxyl ion of approximately 5×10^{-6} M. Hydrogen sulfide is then passed in for a short time, avoiding any considerable excess. If the latter were sufficient to make the solution approximately 0.1 M with respect to total sulfide present ($[S^{--}] + [HS^-] + [H_2S]$) the concentration of hydroxyl ion would still be over 4×10^{-6} M, and the concentration of sulfide ion would be nearly 4×10^{-8} M.

These calculations indicate orders of concentration of sulfide ion very much lower than anything that has been encountered among the precipitating reagents discussed thus far. In fact the situation is unique in analytical chemistry. Even in the case of 0.01 M ammonium hydroxide, whose ionization is repressed by the presence of 4 M ammonium chloride, the concentration of hydroxyl ion is approximately 4×10^{-8} M. This is the concentration of reagent used for the precipitation of the extremely insoluble hydroxides. Yet this is the concentration of sulfide ion used to precipitate the "more soluble sulfides," while the less soluble sulfides form as precipitates with a concentration of sulfide ion of 1.7×10^{-22} M. Mathematically, the effectiveness of such almost inconceivably low concentrations of reagent may be accounted for by the assumption that these sulfides are correspondingly less soluble than any of the other compounds obtained as precipitates. From the point of view of equilibrium considerations these two ideas fit together into a consistent picture. But mechanically the situation is not so satisfactory. It is contrary to all other experience that precipitates should form so readily as the sulfides do when the precipitating ion is added in such low concentrations. It is interesting to note that the anomalous case of the sulfides is based on the assumption that the sulfides are formed as precipitates only by the combining of metallic ion with sulfide ion. If the reaction takes place only in this way then the sulfides must be extremely insoluble. But it is entirely conceivable that

the precipitation occurs through the combining of metallic ion with acid-sulfide ion ($Cu^{++} + 2\ HS^- = Cu(HS)_2$), and that the acid sulfide is sufficiently unstable so that the operations of filtering, washing and drying convert it more or less completely into the normal sulfide ($Cu(HS)_2 = CuS + H_2S$). On this basis one is concerned with the concentrations of acid-sulfide ion,[1] HS^-, as supplied by the hydrogen sulfide under the various conditions of acidity and alkalinity. In the above calculations these data are given. For convenient reference they are re-assembled in Table 11.

TABLE 11

CONCENTRATIONS OF ACID-SULFIDE ION IN VARIOUS SOLUTIONS

Solution	$[HS^-]$
0.1 M H_2S, 0.25 M HCl	3.6×10^{-8}
.1 M H_2S	0.95×10^{-4}
.1 $M([S^{--}]+[HS^-]+[H_2S])$, $[H^+]=1.1\times10^{-7}$	.045
.1 M NH_4HS	.092
.1 M $(NH_4)_2S$	.099

These concentrations of acid-sulfide ion are sufficiently high to make promptness of precipitation entirely rational, mechanically. At the same time it is obvious that the acidity of the solution exerts a very pronounced effect on the concentration of acid-sulfide ion as precipitating agent. On the other hand it is to be noted that only the first power of the concentration of hydrogen ion is involved in the control of the concentration of acid-sulfide ion, in contrast to the second power of the concentration of hydrogen ion as a factor in the control of concentration of sulfide ion

$$[HS^-] = \frac{K_1 \times [H_2S]}{[H^+]}, \qquad [S^{--}] = \frac{K_1 \times K_2 \times [H_2S]}{[H^+]^2}$$

It is beside the point to undertake a discussion of the theory of sulfide precipitation from this point of view. As a matter of fact the experimental data have not as yet been rechecked from this angle, nor has further work been undertaken to justify a mathematical treatment of the situation. It is to be noted, however, that the separations as actually obtained are not affected by this uncertainty as to the mechanism by which the precipitates are formed.

In leaving this discussion of the conditions used for the precipitation of Group IV, attention must be directed again to the fact that a group reagent should precipitate the given group with reasonable completeness and, at the same time, should avoid the precipitation of later group metals. In

[1] G. M. Smith, *J. Am. Ch. Soc.*, **44**, 1500 (1922); Smith and Simon, *J. Am. Ch. Soc.*, **46**, 1325 (1924).

the case of Group IV, nickel sulfide, and to a lesser extent zinc sulfide, show some tendency to redissolve if hydrogen sulfide is passed into the solution for too long a time. This is probably a case of peptization to form a colloidal solution rather than a dissolving by complex-ion formation. It can be avoided by treating the solution with hydrogen sulfide for only a short time, then filtering and testing the filtrate with more hydrogen sulfide for completeness of precipitation; repeating as necessary until the desired ions have been removed. The separation from barium, strontium, calcium and magnesium depends on keeping the concentration of hydroxyl ion fairly low. This is accomplished effectively in the systematic scheme of analysis by the high concentration of ammonium chloride used in the precipitation of Group III. But, if one were concerned with analyzing a solution for only Groups IV and V and neglected to add ammonium chloride before treating the solution with ammonium hydroxide and hydrogen sulfide, several troubles might be encountered. For example, a 0.25 *M* solution of calcium chloride, on being made strongly alkaline with ammonium hydroxide and treated with hydrogen sulfide, slowly forms a coarsely granular, white precipitate of calcium sulfide. Further, magnesium hydroxide precipitates when ammonium hydroxide is added to a solution of magnesium chloride, unless ammonium ion is present in sufficient concentration to keep the concentration of hydroxyl ion low. Still further, an alkaline reagent, such as ammonium hydroxide, will absorb carbon dioxide from the air unless it is very carefully protected from such contamination. The carbon dioxide is neutralized by the hydroxyl ion, forming bicarbonate and carbonate ions, the concentration of the latter depending directly on the concentration of hydroxyl ion present. The ordinary solution of ammonium hydroxide contains sufficient carbonate ion to give a distinct precipitate of calcium carbonate on treatment with calcium chloride. By first adding a high concentration of ammonium chloride this effect can be overcome. Thus, even in the use of hydrogen sulfide in alkaline solution to precipitate the more soluble sulfides, it is necessary to exercise careful control over the conditions employed in order to accomplish the separations desired.

§29. The Reagent Used for the Precipitation of Group V is Carbonate Ion. — The carbonates of barium, strontium and calcium are not extremely insoluble compounds, therefore the concentration of carbonate ion cannot be very low or the precipitation of Group V will be too incomplete to be considered satisfactory. On the other hand, magnesium carbonate is sufficiently insoluble so that if the solution contains a fairly large amount of magnesium part of it will precipitate, unless the concentration of carbonate ion is kept somewhat low. The reagent employed to introduce carbonate ion into the solution is ammonium carbonate, prepared by dissolving the commercial salt in dilute ammonium hydroxide. It is possible to precipitate magnesium quite fully in Group V by using a concentrated

reagent and adding alcohol to reduce the solubility of the magnesium carbonate. In this book, however, a more dilute reagent is used, leaving magnesium to be detected in the filtrate from the carbonate precipitate.

In the case of carbonate ion, as in the case of sulfide ion, there is a definite relation between the acidity or alkalinity of the solution and the concentration of carbonate ion supplied by a given concentration of the reagent. Carbonic acid is relatively unstable and is a weak acid, dissociating in two steps to form bicarbonate ion and then carbonate ion. The ionization constants for these two reactions are:

$$\frac{[H^+] \times [HCO_3^-]}{[H_2CO_3]} = 3.5 \times 10^{-7}$$

$$\frac{[H^+] \times [CO_3^{--}]}{[HCO_3^-]} = 5 \times 10^{-11}$$

If, in the precipitation of Group V, a sufficient excess of reagent is added to make the concentration of ammonium carbonate in the solution 0.1 *M*, it is possible to calculate the concentration of carbonate ion for various concentrations of hydroxyl ion (the assumption being made that ammonium carbonate is a typical salt, largely dissociated into ammonium and carbonate ions). Table 12 gives the results of some of these calculations.

TABLE 12

COMPOSITION OF SOME CARBONATE SOLUTIONS

Solution	$[CO_3^{--}]$	$[HCO_3^-]$	$[H_2CO_3]$
Total carbonate = 0.1 *M* $[H^+] = 1 \times 10^{-6}$	1.3×10^{-6}	0.026	0.074
Total carbonate = 0.1 *M* $[H^+] = 1 \times 10^{-7}$	3.9×10^{-5}	.078	.022
Total carbonate = 0.1 *M* $[H^+] = 1 \times 10^{-8}$	4.8×10^{-4}	.097	.003
Total carbonate = 0.1 *M* $[H^+] = 1 \times 10^{-9}$	5×10^{-3}	.0947	.0003
Total carbonate = 0.1 *M* $[H^+] = 1 \times 10^{-10}$	5×10^{-2}	.05	1.4×10^{-5}

The filtrate from Group IV usually contains approximately 4 *N* ammonium chloride and 1 *N* ammonium hydroxide. Under these conditions the concentration of hydrogen ion is approximately 3×10^{-9}, which would permit a 0.1 *M* carbonate solution to supply a concentration of carbonate ion of 1.6×10^{-3} *M*. Of the three carbonates of Group V, barium precipitates least readily. Its solubility product as reported by McCoy and Smith[1] is 8.1×10^{-9}. On that basis a concentration of carbonate ion of 1.6×10^{-3} *M* should, theoretically, reduce the concentration of barium to

[1] McCoy and Smith, *J. Am. Ch. Soc.*, **33**, 468–73 (1911).

$5 \times 10^{-6} M$, or approximately 0.02 mg. in 25 cc. (The word, theoretically, in the last sentence covers two assumptions: (1) that the solubility product of barium carbonate has the value indicated in this particular solution; and (2) that the barium is present essentially as barium ion instead of molecular salt or complex ion.) Unfortunately, it has been observed that ammonium chloride interferes rather seriously with the precipitation of Group V carbonates, especially in dilute solutions of the metals. The explanation of this effect is commonly assumed to lie in the removal of hydroxyl ion from the carbonate solution by the combining of ammonium ion with hydroxyl ion to form the weak base, ammonium hydroxide, followed by a corresponding conversion of carbonate to bicarbonate ion, so the concentration of carbonate ion becomes too low for satisfactory precipitation of the Group V carbonates. The effect is more marked, however, than it should be if this were the complete story; therefore it appears probable that other factors are also involved, such as possible specific slowness of precipitation of Group V carbonates with low concentrations of carbonate ion, possible formation of intermediate ions ($NH_4CO_3^-$, $BaCl^+$) or complex ions, interionic attraction, etc.

Whatever the complete explanation, the ammonium chloride interference is sufficiently serious so that one must reduce the concentration of this substance very considerably before attempting to precipitate Group V. Several methods of doing this are available. Thus, one may evaporate the solution to dryness and carefully heat the residue until the ammonium chloride fumes no longer appear ($NH_4Cl \rightleftarrows NH_3 + HCl$). Or, one may treat the solution with a large excess of nitric acid and evaporate carefully to approximate dryness ($NH_4NO_3 = N_2O + 2\ H_2O$). Another method of removing ammonium ion consists in adding to the solution an amount of solid sodium bicarbonate slightly more than equivalent to the ammonium salt present, then boiling until the odor of ammonia is no longer observed ($NH_4HCO_3 = NH_3 + H_2O + CO_2$). The carbon dioxide helps to sweep the ammonia out of the solution so the operation proceeds fairly rapidly. It is simple to make sure of completeness of removal of ammonium ion by testing the solution with litmus paper. If excess of sodium bicarbonate was added, this excess was decomposed by heat, giving a solution of sodium carbonate, which is distinctly alkaline. If insufficient sodium bicarbonate was added, and the solution then boiled until no more ammonia could be detected in the vapors, the resulting solution would be neutral or very faintly acid. In such a case more sodium bicarbonate should be added and the operations repeated. In this procedure most of the magnesium as well as the barium, strontium and calcium would precipitate as carbonates. These may be filtered out, washed, dissolved in a small amount of dilute hydrochloric acid, then treated with ammonium hydroxide and ammonium carbonate for the separation of barium, strontium and calcium from magnesium.

In connection with Table 12 showing the composition of carbonate solutions with varying concentrations of hydrogen ion, it should be noted that such solutions are not necessarily stable when exposed to air. This is due to the fact that carbonic acid is rather unstable, breaking down into water and carbon dioxide, the solubility of the latter depending upon the partial pressure of the gas in the air to which the solution is exposed. Thus, Smith[1] gives the following table of molar solubilities.

TABLE 13

SOLUBILITY OF CARBON DIOXIDE AT DIFFERENT PARTIAL PRESSURES

Percentage by volume of CO_2 in gas phase	Pressure of CO_2 in gas phase	Molar solubility of CO_2
0.03	0.218 mm.	1.22×10^{-5}
.09	.654 "	3.7×10^{-5}
100.	760. "	4.07×10^{-2}

The molar solubility of carbon dioxide in salt solutions decreases slightly from the figures given, but one may assume, without serious error, that any aqueous solution in contact with pure air (containing 0.03% of carbon dioxide) will, at equilibrium, contain carbon dioxide to the extent of 1×10^{-5} *M*. This is, of course, partly hydrated to form carbonic acid; but for purposes of this discussion the extent of such hydration is not important. If the sum of the concentrations of carbon dioxide and carbonic acid is less than 1×10^{-5} *M*, then the solution is less than saturated with respect to carbon dioxide at the partial pressure present in the air. If it is greater than 1×10^{-5} *M* the solution is supersaturated with respect to carbon dioxide, and will more or less readily expel this gas into the air. On glancing at Table 12, showing the composition of carbonate solutions, it will be noted that only the last one in the list shows a concentration of carbonic acid of approximately this value. The others are all supersaturated with respect to carbon dioxide and therefore are unstable solutions. Thus a 0.1 *N* carbonate solution requires a concentration of hydrogen ion of slightly less than 1×10^{-10} (or a concentration of hydroxyl ion of slightly more than 1×10^{-4}) in order to be stable in contact with normally pure air. In the case of ammonium carbonate-ammonium hydroxide mixtures the ratio of the concentration of ammonium ion to that of molecular ammonium hydroxide would need to be 1:18 $\left(\frac{[NH_4^+] \times [OH^-]}{[NH_4OH]} = 1.8 \times 10^{-5}\right)$ in order to establish a concentration of hydroxyl ion of 1×10^{-4}. This means that, in addition to the known instability of ammonium hydroxide solutions (due to loss of ammonia into the air), an ammonium carbonate

[1] Smith, T. B., "Analytical Processes," Longmans, Green & Co., New York, **1929**, 144.

solution will lose carbon dioxide. Thus an ammonium carbonate reagent needs to be well stoppered to give it even moderate stability.

§30. The Group System in Acid Radicals. — It will be noticed that in this discussion of group separations only the metals have been considered. The question may well be asked, is the same type of procedure used in testing for acid radicals as for metals; namely, the separation of the anions into a number of groups by precipitation reactions, followed by further separation and identification of the constituent members of the individual groups? The answer to this question is, No![1] If one glances through several texts on qualitative analysis he will find the anions spoken of as belonging in various groups; but if the procedures suggested in testing for these are examined it will become perfectly evident that the term "Group" is not used in the same sense with reference to anions as it is in the case of cations. The discovery of this fact is usually sufficient to raise another question, namely, why not? The answer to this question is found in a consideration of the reasons why there are so few systems of group reagents for the metals.

Any system of group precipitation reagents for the anions, just as in the case of the cations, would necessarily be based on the solubilities of salts. The same salts are available in one case as in the other, therefore it might seem as if the process for the anions would be merely the reverse of that for the cations, using soluble salts of the metals to precipitate various anions instead of soluble salts of the acids to precipitate various of the cations. A further consideration of the varying degrees of stability and extent of ionization of the acids leads to the suggestion that the group separations of the anions should be carried out in alkaline or possibly neutral solution, rather than in acid solution. Only under such conditions will the anions from weaker acids be present in sufficient concentration to precipitate readily with the metallic ions. But, as noted before, an alkaline solution limits in marked fashion the number of metallic ions that may be used as reagents, for many of the metals form insoluble hydroxides. Since the insoluble salts of those metals whose hydroxides are soluble cover only a few of the anions, it is evident that no scheme of group separations among the anions can be worked out on the basis of simple solubility relations. It will be recalled that in the case of the metals, certain groups were formed of extremely insoluble compounds by use of a concentration of precipitating ion sufficiently low to avoid the formation of relatively insoluble compounds having a higher order of solubility than the group precipitated. In these cases the reagent anion was controlled by the presence of a cation with which it would combine to form a slightly ionized compound. The analogous case for group separations among the anions would require that there

[1] The latest attempt to develop a systematic scheme of group precipitation for the anions is that of Duschak and Sneed, *J. Ch. Ed.*, 8, 1177, 1386 (1931).

be cations, forming extremely insoluble compounds among the anions, whose concentration could be controlled by the introduction of anions with which the cations would form slightly ionized compounds. But the metallic salts are typically considered to be highly ionized compounds, so there are relatively few cases in which the condition described can be realized. An examination of these cases in conjunction with a solubility table will show that it is not feasible to work out any useful groups of anions on that basis. And so the conclusion is reached that the anions are not divided into analytical groups in the same way as the metals are, because the properties of the anions and of the available reagents do not make such a grouping possible.

In making this last statement, it must not be thought that this is an entirely unfortunate situation. Attention has been directed frequently to the fact that the systematic separations of groups of metals from each other do not proceed smoothly. Indeed, there are many irregularities in the usual scheme of analysis for metals, such that it is necessary to look for several of them in more than one place, or to modify the confirmatory tests in such a way as to avoid interference by other metals that may be present due to inadequate separations. The group system in qualitative analysis is the outgrowth of that period in the development of analytical chemistry in which the attempt was made to conserve material by making as many tests as possible on a single portion of the sample being analyzed. The difficulty with which accurate results are obtained by this method is generally recognized, so the whole trend in modern analytical chemistry is toward the opposite extreme of making as few tests as possible on a single portion of the material. To do this successfully requires either a relatively large quantity of the material being analyzed or the development of techniques for accurate determinations on very small samples. Progress in the latter direction has been so marked as to result in the recognition of a new division of analytical chemistry to which the name, micro-analysis, is given.

§31. **In the work on acid radicals,** therefore, where necessity forces a departure from the group system of testing, one starts with a relatively large number of individual portions of the original solution and examines each as directly as possible for one or two, or occasionally more, anions. In such procedures it becomes necessary to know what other materials may be present and to take their chemical behavior into account, modifying the procedures as necessary according to the results of individual tests.

Thus, suppose a scheme of analysis were being worked out for the following twelve anions:

arsenate	chlorate	nitrate	sulfate
bromide	chloride	oxalate	sulfide
carbonate	iodide	phosphate	sulfite

For purpose of reference (and for the giving out of unknowns) it might be convenient to subdivide these into three groups.

Group I Anions

Barium and Calcium Salts Insoluble in Water

arsenate	oxalate	sulfate
carbonate	phosphate	sulfite
	(sulfide?)	

Group II Anions

Silver Salts Insoluble in Nitric Acid

bromide	chloride	iodide	(sulfide?)

Group III Anions

Normal Salts Soluble in Water

chlorate	nitrate

In actual analysis, however, little use is made of these groups except to indicate how some separations may be carried out if necessary to avoid certain interferences. Separate portions of the original solution are commonly taken to test for each of the following anions: carbonate, chlorate, nitrate, oxalate and sulfide. The tests for sulfate and sulfite are usually made on a single sample. The same is true for arsenate and phosphate. In the same way one sample usually serves to test for the three halides, iodide, bromide and chloride. It must not be supposed, however, that the tests on these separate portions are always simple direct procedures. In most cases there are possibilities of interference which must be taken into account in the development of individual tests. Because of this fact there is less of routine procedure in the work on anions than in the case of cations. As a consequence, a better general grasp of chemical relations is necessary for the intelligent examination of a solution for anions than for cations.

In the test for a carbonate, for example, the solution is acidified and boiled. This converts any carbonate to carbon dioxide, so that if the vapors are passed into lime water a white precipitate of calcium carbonate is obtained. But one must remember that sulfurous acid is unstable, and that sulfur dioxide will also react with calcium hydroxide to form a white precipitate. Also, that any aqueous solution will normally contain a small amount of carbon dioxide from contact with the air. Still further, that under strong oxidizing conditions oxalic acid is slowly oxidized to carbon dioxide.

The decolorization test for an oxalate depends on the fact that oxalic acid is a mild reducing agent while potassium permanganate is a strong

oxidizing agent. If a few drops of dilute permanganate solution are added to a hot, acid solution containing an oxalate the permanganate will be reduced to manganous ion, with accompanying disappearance of the light red color characteristic of a dilute solution of permanganate ion. Obviously, any reducing agent would produce the same effect. Therefore, if this is to be used to detect an oxalate, it is necessary to carry out a series of operations that will effectively separate this ion from other possible reducing agents before applying the test. These operations commonly include: (1) precipitating with calcium chloride in dilute acetic acid solution, (2) filtering and washing thoroughly, (3) dissolving the calcium oxalate in dilute nitric acid, (4) boiling the solution gently for several minutes, and (5) cooling to approximately 60° before adding the permanganate ion. Further, it is necessary to use a dilute permanganate reagent and add it in small amounts to avoid introducing so much reagent that it will not be completely reduced by such limited quantities of oxalate as one may be interested in identifying. The separation of the oxalate from other reducing agents depends upon several considerations. The precipitate obtained in the acid solution leaves in solution such reducing agents as will not precipitate with calcium chloride under these conditions; including halide, sulfide, arsenite ions, etc. By filtering and washing thoroughly the separation is completed. Nitric acid, used to dissolve the calcium oxalate, usually contains small amounts of nitrous acid, which will reduce permanganate ion, and may be mistaken for an oxalate. But nitrous acid is unstable and easily removed by boiling the solution for a short time, while oxalic acid is oxidized too slowly by dilute nitric acid to be lost in appreciable amounts during this operation, providing reasonable care is taken with respect to the concentration of the nitric acid and the length of time the solution is boiled. Finally, permanganic acid is sufficiently unstable at the boiling point of water so that it is necessary to cool the solution slightly before adding the permanganate in order to avoid loss of color when oxalate is absent.

One more case will be used to illustrate the need of preliminary separations to avoid interferences in tests for anions; namely, the halide-chlorate problem. It is possible to prepare a stable solution containing both halide and chlorate so long as the solution is kept neutral or alkaline. But if such a solution is acidified various reactions will take place more or less readily, involving reduction of the chlorate and oxidation of iodide, bromide, and even chloride. Since the usual tests for the halides are based on successive oxidations in acid solution, it is evident that if a chlorate is present there must be carried out a separation of halide from chlorate before the tests for the individual halides are tried. This may be done by treating a portion of the original solution directly with excess of silver nitrate solution (without acidifying), filtering, washing and finally getting the halides into solution by treatment of the silver salts with metallic zinc in the presence of

dilute sulfuric acid. After allowing ample time for the reaction to take place, the metallic silver and excess of zinc are filtered out, the filtrate being examined for iodide, bromide and chloride ions. In the absence of chlorate these operations are usually unnecessary, therefore it is desirable to test for chlorate before testing for halides. But there is no direct test for a chlorate, the common procedure involving reduction to chloride and identification of that anion. Obviously, if a halide is present it must first be removed; therefore the first operation in testing for a chlorate is the precipitation of any halide by the procedure indicated above.

It will be evident, from the cases discussed, that in testing for anions one is concerned with questions other than solubility relations more frequently than is true in the case of the cations. The additional properties that are most useful[1] in the procedures commonly employed are strength (extent of ionization) and stability of the acids and the readiness of oxidation or reduction of the anions in acid and in alkaline solution.

THE SOLUBILITY PROBLEM IN ANALYTICAL CHEMISTRY

The type of material presented under this topic is not readily available in the standard texts or reference books in chemistry. It is not simple reading, possibly it is more difficult than should be attempted in a second course in chemistry. It is so closely concerned, however, with the problems of chemical analysis that it has been included at this point in the hope that it may help the student to orient himself in that field.

§32. In discussing separations by precipitation processes as usually employed in analytical chemistry, the statement is frequently made that these involve merely differences in solubility. The implication is obvious, that solubility is a simple, easily determined quantity with which the chemist is perfectly familiar. This attitude may be warranted in an introductory course in chemistry, but it hardly seems fair to the student who is continuing the subject to leave him with this lack of appreciation of the complexity of the question of solubility, the difficulty of its experimental determination under controlled conditions, and the uncertainty in the interpretation of experimental results once they are obtained.

One needs only a glance into the literature of solubility determinations to realize that the situation is by no means simple. Compare, for instance, the values reported by two different workers for the solubility of barium

[1] The article by Pierce, *J. Ch. Ed.*, **8**, 1858 (1931), shows some of the various tests for groups of anions.

sulfate in various concentrations of nitric acid. (See Table 14.) Individually, the papers in which these two sets of results are reported are fairly convincing, and yet when the two are compared the solubilities in the one range from 1.9 to 4.2 times as great as those in the other. Or, compare the discordant sets of figures for the solubilities of the sulfides. (See Table 15.)

TABLE 14

SOLUBILITY OF $BaSO_4$ IN HNO_3

Concn. of HNO_3 N	G. $BaSO_4$ per 1000 cc. as reported by		Ratio $\frac{A}{B}$
	A*	B†	
0.05	0.017	0.009	1.9
.10	.027	.012	2.2
.50	.098	.039	2.5
1.00	.237	.077	3.1
2 00	.502	.119	4 2

* Karaoglanow, *Z. anal. Ch.*, **56**, 228, 245 (1917).
† Kolthoff and Vogelenzang, *Ibid.*, **58**, 54 (1919). (In the original paper an error in the decimal place made the values appear one-tenth those given in this table.)

TABLE 15

SOLUBILITIES OF SULFIDES

Sulfide	Molar solubility as reported by		Ratio $\frac{A}{B}$
	A*	B†	
MnS	7.2×10^{-6}	2.6×10^{-8}	280
CdS	8.9×10^{-6}	2.7×10^{-14}	3.3×10^{8}
CuS	3.5×10^{-6}	1.1×10^{-21}	3.2×10^{15}

* Weigel, *Z. physik. Ch.*, **58**, 293–300 (1907).
† Bruner and Zawadzki, *Z. anorg. allgem. Ch.*, **65**, 136–51 (1909).

In examining such figures it is necessary to remain critical rather than assuming that one is right and the other wrong. Probably both represent correct experimental results for the conditions under which the work was done. It is possible also that errors in procedures or in assumptions may invalidate both sets of data.

Sometimes it is possible to use supplementary information to help in deciding the relative accuracy of two such sets of data. Thus, the separations in qualitative analysis by means of controlled acidity while precipitating Group II with hydrogen sulfide, find a more adequate basis in the

solubilities of the sulfides as reported by Bruner and Zawadzki than in those of Weigel. The figures of Weigel show only an eightfold difference in solubilities of manganese and cadmium sulfides, hardly sufficient to account for the difference in readiness of precipitation in dilute acid solution. The figures of Bruner and Zawadzki, however, show a million fold difference in solubilities of the two sulfides, entirely sufficient to account for the effect under consideration. But it is to be noted that there are other factors beside solubility that play a part in the readiness with which a precipitate forms, some compounds showing more marked supersaturation effects than others. It is, therefore, hardly fair to use analytical separations as the criterion of relative solubilities and then to say that the separations are based on these differences in solubility.

For substances of moderate solubility there is no very serious difficulty in obtaining reasonably concordant data that can be checked by other workers. The problem involves the preparation of the pure compound itself, shaking it with pure water under controlled conditions for a sufficient length of time to prepare a saturated solution, and finally, the analysis of the saturated solution. If the compound is of sufficient stability, the last step may be accomplished by merely evaporating a measured portion of the solution to dryness and weighing the residue. In other cases the concentration of one of the radicals of the salt may be determined by gravimetric precipitation or by volumetric titration and, assuming that the other radical is present in equivalent amount, the solubility of the compound obtained by simple calculation. The errors due to slight solubility of glass from the vessels in which the operations are carried out, and to reaction of the salt with water (hydrolysis, etc.) are usually small enough in comparison with the quantity being determined to be regarded as negligible.

In analytical chemistry, however, one is interested in substances of relatively low solubility, and for these the errors mentioned will frequently be as great as, or greater than, the quantity being determined. In such cases the data will indicate an order of magnitude that permits the classification of a compound as slightly soluble, moderately insoluble, etc., but will not permit adequate distinctions among compounds of the lower orders of solubility.

The attempts to determine the solubility of difficultly soluble substances have been indirect for the most part, involving the measurement of some property of the saturated solution and then calculation of the solubility by the application of a formula which may have an empirical or a theoretical basis.

Departing from the usual custom of selecting from the more or less discordant values reported in the literature a somewhat arbitrary list of data for a solubility table, it has seemed worth while to try the experiment of reporting in some detail several of the studies in this field. It is hoped, in this way, to give the student a better appreciation of the experimental

basis of the figures reported, the sources of error, and the possible accuracy of the results.

It would require many pages to cover with some degree of completeness the experimental methods that have been employed in determining the solubilities of slightly soluble substances. In the limited space available the discussion will cover only six pieces of work in this field. These are the studies (1) by Kohlrausch on salts of the stronger bases and acids, (2) by Böttger on salts of silver, lead and thallium, (3) and (4) by Weigel and by Bruner and Zawadzki on sulfides, and (5) and (6) by Remy and Kuhlmann and by Britton on hydroxides. The following outline may help the student find his way through this section. Each paper is presented in extended outline, showing the experimental method employed, the data obtained, the method of calculating solubilities from the experimental data, and the solubilities as finally calculated. Following papers 2, 4 and 6, comparisons are made with the immediately preceding papers, and where results are discordant some attempt is made to account for the differences. In conclusion two questions are raised and discussed in the light of the papers presented, (1) how definitely are the solubilities of slightly soluble substances known, (2) to what extent is a solubility table useful in analytical chemistry?

§33. One of the more extensive pieces of work in this field is that of Kohlrausch. Starting in 1890, and continuing with the aid of several co-workers over a period of 13 years, the results were published in two main articles in the Zeitschrift für physikalische Chemie, for the years 1903 and 1908. Part I, 42 pages in length, covers the experimental determination of the electrical conductance of saturated solutions of 41 substances at a moderate range of temperatures. Part II, 40 pages in length, deals with the calculation of solubility, and its change with temperature, from the experimental data of Part I. The salts studied are listed in Table 16.

TABLE 16
SALTS STUDIED BY KOHLRAUSCH

Metals	Acid radicals										
	Cl^-	Br^-	I^-	F^-	CNS^-	IO_3^-	SO_4^{--}	CrO_4^{--}	$C_2O_4^{--}$	CO_3^{--}	OH^-
Ba....	....	....	....	BaF_2	....	....	$BaSO_4$	$BaCrO_4$	BaC_2O_4	$BaCO_3$	....
Sr....	....	....	....	SrF_2	....	....	$SrSO_4$	....	SrC_2O_4	$SrCO_3$	....
Ca....	.. .	....	....	CaF_2	....	....	$CaSO_4$	$CaCrO_4$	CaC_2O_4	$CaCO_3$	....
Mg...	....	....	....	MgF_2	....	....	....	....	MgC_2O_4	$MgCO_3$	$Mg(OH)_2$
Zn....	....	....	....	ZnF_2	....	....	....	....	ZnC_2O_4	....	....
Cd....	....	....	....	....	....	....	....	....	CdC_2O_4	....	....
Ag...	AgCl	AgBr	AgI	....	....	$AgIO_3$	....	Ag_2CrO_4	$Ag_2C_2O_4$	....	....
Cu....	....	....	CuI	....	CuCNS	....	....	....	....	....	....
Tl....	TlCl	TlBr	TlI	....	....	....	....	....	....	....	....
Hg....	HgCl	....	HgI_2	.. .	....	....	....	....	....	....	....
Pb....	....	....	....	PbF_2	....	$Pb(IO_3)_2$	$PbSO_4$	$PbCrO_4$	PbC_2O_4	$PbCO_3$	....

The salts studied were commonly prepared by precipitation from recrystallized, or otherwise purified, materials, and then washed for extended periods of time with distilled water. From this point on two procedures were adopted. Sometimes the salt was dried and rubbed to a fine powder in an agate mortar; sometimes the salt was ground without drying, and preserved moist. In most cases measurements were carried out using both types of material. Occasionally specimens of unusually pure minerals were used as additional samples such as, fluorspar (CaF_2), barite ($BaSO_4$), celestite ($SrSO_4$), gypsum ($CaSO_4 \cdot 2H_2O$), calcite and aragonite ($CaCO_3$).

The resistance cells used were small cylindrical flasks of 15–50 cc. capacity, provided with platinum electrodes of 5–8 cm.^{2} size and far enough apart so that with the flask filled with a solution having unit specific conductance the resistance of the cell would be 0.1–0.15 ohm. The glass stoppers of the flasks carried thermometers with the mercury bulbs lying between the electrodes. To avoid error due to suspensions of solid particles of the salt, if the latter happened to be a conductor as in the case of the silver halides, ample space was left between the lower edge of the electrodes and the bottom of the flask so that these particles might settle out of the stronger electrical field before measurements were made. In the case of substances of very low solubility this becomes increasingly important, the values for AgBr and AgI being respectively twofold and tenfold too high in the measurements made before the need of this precaution was recognized.

The preparation of the saturated solution was carried out in the resistance cell itself. In this way any irregularities due to filtration, transfer of saturated solution, and exposure to air over somewhat protracted intervals were avoided. At the same time the approach to saturation could be followed by making measurements of the resistance of the cell from time to time. So long as the resistance is decreasing the concentration of the solution is increasing, and when a minimum is reached the solution has become saturated. Since stirring or shaking decreases the time necessary for preparation of a saturated solution provision was made for rotating the flask on a horizontal axis by clamping the thermometer into a brass tube attached to the center of a wheel that could be turned by a small electric motor.[1]

A quantity of the finely powdered salt was transferred to the cell sufficient to saturate many times the volume of water contained in the cell. The cell was then filled with water, leaving a small air bubble to assist in agitating the solution, shaken for measured intervals of time, and the changes in resistance followed by means of measurements of the Wheatstone bridge type. When a minimum resistance was finally reached the solution was removed by decanting or syphoning, then a fresh portion of

[1] See *Z. physik. Ch.*, **44**, 203 and 204 (1903), for illustrations of cells and rotating mechanism.

water was added, and the process repeated. These operations were continued until it was certain that further treatments with water would give the same results as had already been reached.

Frequently the first few solutions prepared would show fairly low resistances, increasing later to reasonably constant values. Such effects were considered to indicate the presence of soluble impurities in the salt, probably adsorbed from the reagents used in the original preparation and incompletely removed in the earlier washing. Sometimes these impurities were very persistent, requiring prolonged and repeated soaking for their removal. The following cases showed marked difficulty of this type: (1) BaF_2, precipitated cold from $BaCl_2$ with excess of KF, (2) MgF_2, precipitated from $MgSO_4$ with KF, (3) CuI, precipitated from $CuSO_4$ with excess of KI in the presence of H_2SO_3, (4) $Pb(IO_3)_2$, precipitated from $Pb(NO_3)_2$ with $NaIO_3$, (5) MgC_2O_4, precipitated with $Na_2C_2O_4$, (6) ZnC_2O_4, precipitated from $ZnSO_4$ with $Na_2C_2O_4$, and (7) PbC_2O_4, precipitated with $Na_2C_2O_4$. Thus in the case of the magnesium oxalate mentioned, after the usual washing and drying, the fine powder was soaked for 20 days in water at room temperature, then digested at 28° for 3 days. Following this, a fresh treatment with water gave a distinct test for sodium after 2 days and in 17 months showed a resistance less than a tenth that which was finally selected as characteristic of a saturated solution of the pure salt. Again, in the case of the magnesium fluoride, following the usual washing, eight successive treatments with water for 2-hour periods each still gave resistances about 0.4 that finally selected, and the solutions gave distinct tests for sulfate with barium chloride. The figures were inserted in the original paper as an illustration of unusually persistent impurity in a precipitated salt.

Early in the study it was found desirable to vary the temperature of the solution within moderate limits, from somewhere near 0° to slightly over 30°. This made it possible to study the change of solubility with temperature, and was frequently an important means of deciding when the solution had become saturated. For substances that dissolved rapidly this last matter caused little trouble, but for substances that dissolved slowly the situation was different. In the latter case there was always the question whether the solution had actually become saturated or whether the dissolving was taking place so slowly that the time interval between measurements was too small to show the change that was occurring. If there is an appreciable change in solubility with temperature, a change of temperature of the solution while rotating in contact with fine particles of the salt should produce a change in resistance different from that calculated from the temperature coefficient of the clear solution with no solid salt present. If on restoring the original temperature the original resistance was again observed, the solution was saturated; if a different resistance was observed the solution was not in equilibrium with the solid salt. For

salts whose solubility is not affected appreciably by the temperature this criterion fails; which is to be regretted since these very substances usually dissolve so slowly that one is in doubt as to whether impurities are playing a part in the change in resistance.

The quantities actually measured were resistances at particular temperatures. These were converted to conductances by the simple formula

$$C = \frac{1}{R}$$

in which C = conductance, and R = resistance. The specific conductance was then calculated by multiplying the conductance, C, by a conversion factor called the *cell constant;* the latter having been previously determined for the cell used by measuring its resistance when filled with a solution of known specific conductance. (The specific conductance of a solution is that measured between parallel electrodes each 1 sq. cm. in area, and 1 cm. apart.) In each case the specific conductance (γ) of the water used was determined as well as that of the solution, and the former was subtracted from the latter to obtain the specific conductance due to the salt in the solution. For this last quantity Kohlrausch used the symbol, $\mathfrak{k}$ (the German letter for k), with a subscript, t, to indicate a temperature other than 18° at which the solution was saturated and the conductance measured.

In addition to a series of measurements on solutions saturated at approximately 18° from which the value for 18° was obtained, two other series of measurements were made to study temperature effects. One, using clear, nearly saturated solutions, gave the basis for calculating the values of the constants (α and β) in the following equation,

$$\mathfrak{k}_t = \mathfrak{k}_{18}[1 + \alpha(t - 18) + \beta(t - 18)^2]$$

used to show the change with temperature in conductance of a solution of constant concentration. The other, using solutions saturated at the different temperatures, made it possible to calculate the change in solubility with temperature.

One of the early difficulties encountered was found in the solvent action of the water on the glass resistance cell. This caused a slow rise in conductance of the water so that the water correction became rather uncertain. It was found that with use the magnitude of this effect decreased, the glass surface becoming more and more resistant to the water. Thus, one of the best cells (made of Jena thermometer glass No. 16) became sufficiently resistant in a year and a half so that a silver chloride solution in 4 days time — during which temperatures from 4° to 30° were used — changed only 0.02×10^{-6} reciprocal ohms. The attempt was usually made to determine the change in the water correction, particularly after experiments

at moderately high temperatures, by repeating the conductance determination of the solution at some lower temperature already used and ascribing any change observed to the water. Thus, in the example given in detail by Kohlrausch, the original conductance of the water used was 1.51×10^{-6}, but after experiments at 40° and at 26.7° the measurement at 18° was 0.49×10^{-6} higher than before (for the saturated solution = 36.64×10^{-6} instead of 36.15×10^{-6}) so the conductance due to the water was considered to have changed to 2.00×10^{-6} reciprocal ohms.

The results of the experiments were expressed in terms of specific conductances of the saturated solutions at 18° with the water conductances subtracted. In most cases there were included values derived experimentally (occasionally calculated from the temperature coefficients of the ions) for the constants α and β, in the equation used to calculate the specific conductance at 18° ($\mathfrak{k}_{t,18}$), of a solution having a specific conductance of $\mathfrak{k}_t$ at some other temperature (t). This calculation served to put data obtained at different temperatures on a common basis so that the solubilities at the different temperatures could be compared. Finally there were given series of specific conductances, at different temperatures, of solutions saturated at those temperatures.

It would be out of place in the present book to include even a summary of the experimental data of this first paper, but a few examples to illustrate the nature of the results have been placed in Tables 17–19.

The usual solubility table gives only the values finally selected to show the concentration of the solution when saturated with the salt at the chosen temperature. But these data tell nothing of the ease or difficulty with which a saturated solution is prepared, the rapidity or slowness with which equilibrium is set up from a condition of under- or super-saturation. In working with actual substances this information may become very important. A few sets of data have been included to illustrate the enormous range of differences in these respects. These are self-explanatory and are found in the tables cited.

For the salts in Table 19 the rates of dissolving (a), and the rates of precipitation from supersaturated solutions (b), were described as follows: BaF_2, (a) slow, (b) slow; AgCl, (a) rapid, (b) rapid; $BaSO_4$, (a) fairly rapid, (b) fairly rapid; CaC_2O_4, (a) fairly rapid, (b) slow.

In the second paper Kohlrausch dealt with the problem of conversion of specific conductances to concentrations. This can be done readily enough if one knows the equivalent conductances of the salt in question, the normality (N) of the solution being related to specific conductance ($\mathfrak{k}$) and equivalent conductance (Λ) by the following formula:

$$N = \frac{\mathfrak{k} \times 1000}{\Lambda}$$

TABLE 17

Variation in Specific Conductance with Different Water Treatments and with Time

Salt	Water treat-ment No.	Values of $\mathfrak{k}_{18} \times 10^6$ after varying time intervals						
$CaCrO_4$	1	11 min. 1070	6 hrs. 1520	33 hrs. 2370	8 days 3090	47 days 9700	360 days 14,900	15,400 days 154,000
MgF_2	1	3.5 hrs. 254						
Value selected for $\mathfrak{k}_{18} \times 10^6 =$ 224	2	15 hrs. 214	48 hrs. 223					
	3	12 hrs. 215	100 hrs. 236					
	4	14 hrs. 205	28 hrs. 219	54 hrs. 227	122 hrs. 234			
	5	5 min. 56	2 hrs. 161	14 hrs. 201	26.5 hrs. 213.5	50 hrs. 221.7	60 hrs. 223.7	120 hrs. 228.8
PbF_2	1	0.5 hr. 445						
Value selected for $\mathfrak{k}_{18} \times 10^6 =$ 431	2	0.5 hr. 435						
	3	5 min. 429						
	4	0.5 hr. 433						
	5	0.5 hr. 431						
	6	0.5 hr. 430	7 days 432					

TABLE 18

Several Cases Showing Slowness of Precipitation from a Condition of Supersaturation

Salt	Original concn.	Change in concentration with time						
BaC_2O_4	$\mathfrak{k}_{18} \times 10^6$ 103	1 min. 98.2	2 min. 93.4	5 min. 85.8	10 min. 80.8	20 min. 77.6	40 min. 76.1	∞ 75
$CaCrO_4$	$\mathfrak{k}_{18} \times 10^6$ 39,160	5 days 39,070	12 days 38,980	∞ 15,400				
MgC_2O_4	normality 0.2	24 hrs. 0.05 *N*	48 hrs. 0.02 *N*	300 hrs. 0.008 *N*	∞ 0.0054 *N*			

TABLE 19

TYPICAL RESULTS IN THE FIRST PAPER BY KOHLRAUSCH

Salt	Preparation* No.	$\mathfrak{k}_{18} \times 10^6$	α	β	$\mathfrak{k}_t \times 10^6$†			
BaF_2	1	1530	0.0232	0.00011	9.50° 1241	17.23° 1520	25.75° 1847	
AgCl	9	1.12	.0222	.00008	1.55° 0.37	10.90° 0.76	17.33° 1.18	33.68° 3.16
$BaSO_4$	21	2.4	.0232	.0001	0.77° 1.10	17.90° 2.35	27.75° 3.30	
CaC_2O_4	44	9.6	.0238	.0001	0.46° 4.30	16.4° 9.00	35.8° 17.99	

* The numbers refer to the individual preparations used and the order in which they were studied.

† Many more data were usually given for each of the salts than are included here.

The problem, then, is to find values for Λ to be used in the calculations. Unfortunately, values for Λ can only be obtained from measurements of $\mathfrak{k}$ in solutions for which the concentrations, N, are known. In the cases of salts of sufficient solubility it is possible to prepare solutions of known concentration, measure $\mathfrak{k}$, and calculate Λ. Since Λ varies with the concentration, it is necessary to measure it at a number of different concentrations approaching saturation and then extrapolate from these to the value characteristic of the saturated solution. This procedure was followed in a number of cases, such as: BaF_2, PbF_2, BaC_2O_4, MgC_2O_4, $CaSO_4$, etc. But for substances of lower solubility, where accurate independent determination of the concentrations of the experimental solutions is impossible, this procedure fails.

In the latter case it is necessary to use the sum of the mobilities of the ions, assuming that the error in the value of Λ is negligibly small (as is done in much of the work after Kohlrausch), or calculating corrections to be applied from the decrease in conductance of similar (but more soluble) salts at the concentrations involved. Experimental studies of many salts indicated that the change in conductance of the salt with concentration might be expressed by the general formula

$$\Lambda_N = \Lambda_\infty - C\sqrt{N}$$

in which Λ_N is the equivalent conductance of the salt at the concentration N, Λ_∞ is the equivalent conductance at infinite dilution (the sum of the mobilities of the ions), and C is an empirical constant characteristic of the salt in question. For BaF_2, PbF_2, BaC_2O_4, and MgC_2O_4, the values of C

are, respectively, 160, 300, 584, and 1670. For salts of univalent ions the same formula applies, C being a constant for each particular ion. The values of these constants for a few of the univalent ions are:

K^+	Ag^+	Tl^+	Cl^-	F^-	IO_3^-
40	42	50	40	34	35

For bivalent ions, however, the situation is much more complex, varying to such an extent that each salt must be considered individually.

It would be out of place to include here an extended discussion of the way in which all the values for Λ were selected for the various salts. It is appropriate, however, to note that Kohlrausch considered the values in general to be accurate to within approximately 1%, occasionally to only 15%. With the values of Λ finally decided upon, the conductance data were converted to concentrations with the aid of the formula given above.

TABLE 20

SOLUBILITIES OF SLIGHTLY SOLUBLE SALTS, ACCORDING TO KOHLRAUSCH

Salt	Λ_∞	Λ_N	$N \times 10^3$ at 18°	Salt	Λ_∞	Λ_N	$N \times 10^3$ at 18°
BaF_2	103.	83.6	18.3	$CaSO_4$	...	63.3	29.7
SrF_2	99.3	92.3	1.864	$PbSO_4$	...	120.7	0.268
CaF_2	99.3	96.2	0.386	$BaCrO_4$	...	115.	0.028
MgF_2	...	79.9	2.8	Ag_2CrO_4	126.	122.8	0.152
ZnF_2	...	...	...	$PbCrO_4$	...	130.	0.0008
PbF_2	108.1	82.3	5.24	$BaCO_3$	...	102–106	0.2
AgCl	119.8	119 5	0 00937	$SrCO_3$	...	102–106	0.15
TlCl	...	118.4	12.78	$CaCO_3$	...	102–106	0.26
HgCl	...	160.	0.009	$MgCO_3$	...	...	...
AgBr*	...	130.	0.00058	$Mg(OH)_2$	...	...	...
TlBr	...	129.	1.49	$PbCO_3$	...	...	0.01
AgI*	...	128.	0.000016	BaC_2O_4	120	103.8	0.755
TlI	...	131.1	0.17	SrC_2O_4	116.7	102.9	0.525
CuI	...	...	...	CaC_2O_4	116.7	110.9	0 0865
HgI_2	...	...	0.001–0.002	MgC_2O_4	111.	37.	5.4
CuCNS	...	...	...	ZnC_2O_4	111.	95.8	0.0835
$AgIO_3$	88.2	87.3	0.136	CdC_2O_4	111.	80.4	0.336
$Pb(IO_3)_2$	94.9	93.3	0.064	PbC_2O_4	135.	120.	0.0108
$BaSO_4$	...	121.7	0.0197	$Ag_2C_2O_4$	124.9	114.5	0.223
$SrSO_4$	...	102.0	1.245				

* For AgBr and AgI the temperatures were 21.1° and 20.8°.

Λ_∞ is the sum of the mobilities of the ions, Λ_N is the equivalent conductance of the saturated solution, and N is the normality of the solution. The temperature was 18° except in the cases of AgBr and AgI.

§34. In the same year as the first of these extensive papers by Kohlrausch, there appeared a paper by Böttger[1] presenting a similar study of

[1] Böttger, *Z. physik. Ch.*, **46**, 520–619 (1903).

a fairly large number of slightly soluble salts of the three metals, silver, thallium and lead. In addition to measurements and observations of the type made by Kohlrausch, chemical determinations of concentrations were made for many of the more soluble salts, thus giving an independent check on the values calculated from conductances.

Table 21 gives the solubilities as determined by Böttger at approximately 20°, with an additional column giving the values obtained by Kohlrausch at 18° where the two lists overlap. It will be noted that the values obtained by the two workers are very similar, even closer than the figures given if the difference in temperatures is taken into account. The only divergent case is that of $PbCO_3$, and for this salt Böttger reported another preparation with a solubility of 8.3×10^{-6}, while Kohlrausch considered the knowledge of the condition of the salt in the solution too uncertain to make accurate calculation possible.

TABLE 21

SOLUBILITIES OF SLIGHTLY SOLUBLE SALTS, ACCORDING TO BÖTTGER

Salt	Equivalents per liter		Salt	Equivalents per liter	
	Böttger, $t = 20°$	Kohlrausch, $t = 18°$		Böttger, $t = 20°$	Kohlrausch, $t = 18°$
$CaSO_4$	2.99×10^{-2}	2.97×10^{-2}	$TlBrO_3$	9.95×10^{-3}	.....
AgCl	1.06×10^{-5}	0.937×10^{-5}	$TlIO_3$	1.52×10^{-3}	.....
AgBr	4.5×10^{-7}	5.8×10^{-7}	$Tl_2C_2O_4$	6.35×10^{-2}	.....
AgCNS	8.2×10^{-7}	.....	Tl_2S	0.86×10^{-3}	.....
AgCN	1.64×10^{-6}	.....	$PbCl_2$	6.92×10^{-2}	.....
$AgBrO_3$	6.7×10^{-6}	.....	$PbBr_2$	4.55×10^{-2}	.....
$AgIO_3$	1.5×10^{-4}	1.36×10^{-4}	PbI_2	2.61×10^{-3}	.....
Ag_2O	1.8×10^{-4}	.....	$Pb(CNS)_2$ ..	2.79×10^{-2}	.....
$Ag_2C_2O_4$	2.4×10^{-4}	2.23×10^{-4}	$Pb(BrO_3)_2$ ..	5.78×10^{-2}	.....
Ag_3PO_4	4.6×10^{-5}	.....	$Pb(IO_3)_2$	6.57×10^{-5}	6.4×10^{-5}
TlCl	1.36×10^{-2}	1.28×10^{-2}	$PbO \cdot xH_2O$ ..	1×10^{-4}	.....
TlBr	1.64×10^{-3}	1.49×10^{-3}	$PbCO_3$	1.3×10^{-6}	1×10^{-5}
TlI	1.92×10^{-4}	1.7×10^{-4}	PbC_2O_4	1.22×10^{-5}	1.08×10^{-5}
TlCNS	1.2×10^{-2}	.....	$PbSO_4$	2.76×10^{-4}	2.68×10^{-4}

§35. The next extensive solubility study to which attention will be called is that of Weigel.[1] Twenty-eight specimens of heavy metal sulfides were studied, some of them native minerals, others artificial minerals prepared in the laboratory, and still others the ordinary precipitates carefully prepared and washed thoroughly with specially distilled water before using in a determination. Fourteen of the common metals were covered, including those of Groups II and IV, silver of Group I, and iron of Group III.

[1] Weigel, *Z. physik. Ch.*, **58**, 293–300 (1907), and reported in greater detail in the *Nachrichten der Kaiserliche Gesellschaft der Wissenschaften*, **1906**, 525–40.

The solubilities were determined at 18° in a saturating apparatus of the same type as was employed by Böttger. In carrying out the experiments the finely divided sulfide was washed for several days with conductance water, then placed in the saturating flask where it was washed several more times by decantation with conductance water. Then the flask was filled with fresh water, and rotated at constant temperature, measuring the conductance from time to time until no further increase could be detected. Most of the determinations were repeated to make certain of the accuracy of the result. The conductance of the pure water was usually determined in the saturating flask before carrying out an experiment; at times the sulfide in the flask was carefully covered with water and the conductance of the latter measured before shaking. Then the solution was rotated at constant temperature. Measurement of the conductance from time to time gave information as to the progress of the dissolving, and the experiment was ended only when no increase in conductance was observed after a moderate interval. The time necessary to saturate the solution varied with the different sulfides, ranging from a few minutes to several days — in the case of a fused FeS 10 weeks were required.

With the specific conductances of the water and of the solution measured, the next problem was to calculate the concentration of the solution. The first step was the usual one of subtracting the specific conductance of the water from that of the solution, the difference being taken as the quantity characteristic of the salt in question. Next, since the sulfides are all highly insoluble, it was considered sufficiently accurate to use the sum of the ionic mobilities for the equivalent conductance of the salt in question. And, finally, it was recognized that hydrogen sulfide is a very weak acid so the sulfides in dilute solution would be largely hydrolyzed. Assuming that the reaction, $S^{--} + 2\,H_2O \rightarrow H_2S + 2\,OH^-$, would occur with some approximation to completeness and that the conductance due to the H_2S would be negligible, the equivalent conductances used in the calculations were the sum of the ionic mobilities of the metallic ion and of the hydroxyl ion.

For ionic mobilities the following values were used: $OH^- = 174$, $\frac{1}{2}\,Pb^{++} = \frac{1}{2}\,Sn^{++} = 61.5$, $\frac{1}{2}\,Hg^{++} = \frac{1}{2}\,Cd^{++} = 47.4$, $Ag^+ = 54.5$, $\frac{1}{2}\,Cu^{++} = 49$, $\frac{1}{2}\,Zn^{++} = \frac{1}{2}\,Fe^{++} = \frac{1}{2}\,Ni^{++} = 47$, $\frac{1}{2}\,Co^{++} = \frac{1}{2}\,Mn^{++} = 45$, $\frac{1}{3}\,As^{+3} = \frac{1}{3}\,Sb^{+3} = \frac{1}{3}\,Bi^{+3} = 85$.

To calculate the concentration of a saturated solution of lead sulfide (assuming complete hydrolysis to lead hydroxide and hydrogen sulfide, the former completely ionized and the latter non-ionized) if the specific conductance of the saturated solution was 1.679×10^{-6}, and that of the water was 1.112×10^{-6},

$$\frac{(1.679 \times 10^{-6} - 1.112 \times 10^{-6})1000}{61.5 + 174} = N$$

This is the concentration of the solution in gram equivalents per liter. To convert to moles per liter this value is divided by 2 (the number of gram equivalents in one mole of lead sulfide).

The data in Table 22 include only the precipitated sulfides since these are the ones of immediate interest in analytical chemistry.

TABLE 22

SOLUBILITY OF HEAVY METAL SULFIDES ACCORDING TO WEIGEL

Sulfide	Time for saturation	Specific conductance of water	Specific conductance of solution	Increase	Molar solubility of sulfide
PbS	5 hrs.	1.230×10^{-6}	2.922×10^{-6}	1.692×10^{-6}	3.60×10^{-6}
HgS	20 min.	1.200×10^{-6}	1.224×10^{-6}	0.024×10^{-6}	0.054×10^{-6}
Ag_2S	30 min.	1.142×10^{-6}	1.394×10^{-6}	0.252×10^{-6}	0.55×10^{-6}
CuS	24 hrs.	1.140×10^{-6}	2.703×10^{-6}	1.563×10^{-6}	3.51×10^{-6}
CdS	20 hrs.	1.206×10^{-6}	5.194×10^{-6}	3.988×10^{-6}	8.86×10^{-6}
ZnS	12 hrs.	1.368×10^{-6}	32.60×10^{-6}	31.23×10^{-6}	70.6×10^{-6}
NiS	13 hrs.	1.078×10^{-6}	18.70×10^{-6}	17.62×10^{-6}	39.87×10^{-6}
CoS	10 hrs.	1.404×10^{-6}	19.64×10^{-6}	18.23×10^{-6}	41.62×10^{-6}
FeS	4 hrs.	1.260×10^{-6}	32.24×10^{-6}	30.98×10^{-6}	70.1×10^{-6}
MnS	90 min.	1.261×10^{-6}	32.60×10^{-6}	31.34×10^{-6}	71.6×10^{-6}
SnS	7 hrs.	1.050×10^{-6}	1.118×10^{-6}	0.068×10^{-6}	0.14×10^{-6}
SnS_2	24 hrs.	1.206×10^{-6}	1.738×10^{-6}	0.532×10^{-6}	1.13×10^{-6}
As_2S_3	10 hrs.	1.200×10^{-6}	4.463×10^{-6}	3.263×10^{-6}	2.1×10^{-6}
Sb_2S_3	11 hrs.	1.224×10^{-6}	9.23×10^{-6}	8.006×10^{-6}	5.2×10^{-6}
Bi_2S_3	11 hrs.	1.480×10^{-6}	2.017×10^{-6}	0.537×10^{-6}	0.35×10^{-6}

From the figures given by Weigel for the sulfides as compared with those for other salts by Kohlrausch and by Böttger it appears that the sulfides generally are less soluble than most of the common salts of low solubility. There is not sufficient difference indicated, however, to account for the readiness with which certain reactions take place — the conversion of the silver halides to silver sulfide, for instance, by treatment with ammonium sulfide. A critical discussion of the paper will be postponed, however, until after the next study in solubilities has been presented.

§36. In 1909 there appeared a paper by Bruner and Zawadzki[1] under the title, "Concerning the Equilibria in the Precipitation of Metals with Hydrogen Sulfide." In this piece of work the problem of solubility was attacked indirectly through the solubility product principle and the law of mass action.

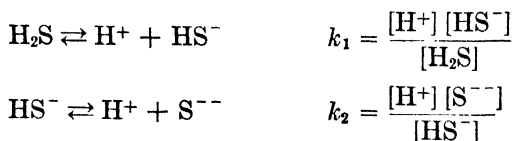
Assuming that a sulfide of the type Me_2S dissociates into 2 Me^+ and S^{--} and that the solubility product principle applies to all aqueous solutions of Me_2S; in any saturated solution

$$L_{Me_2S} = [Me^+]^2[S^{--}]$$

[1] Bruner and Zawadzki, *Z. anorg. allgem. Ch.*, **65**, 136–51 (1909); and in distinctly greater detail in *Bull. intern. acad. polonaise*, **1909**, 267–321.

Hydrogen sulfide dissociates in two stages, with characteristic ionization constants for each:

$$H_2S \rightleftarrows H^+ + HS^- \qquad k_1 = \frac{[H^+][HS^-]}{[H_2S]}$$

$$HS^- \rightleftarrows H^+ + S^{--} \qquad k_2 = \frac{[H^+][S^{--}]}{[HS^-]}$$

From the k_1, k_2 equations

$$[S^{--}] = \frac{k_1 \times k_2 \times [H_2S]}{[H^+]^2}$$

Substituting this in the expression for the solubility product of M_2S

$$L_{Me_2S} = \frac{[Me^+]^2 \times k_1 \times k_2 \times [H_2S]}{[H^+]^2}$$

or

$$\frac{[Me^+]^2[H_2S]}{[H^+]^2} = \frac{L_{Me_2S}}{k_1k_2} = K_1$$

For sulfides of the type MeS, the corresponding constant is K_2:

$$K_2 = \frac{[Me^{++}][H_2S]}{[H^+]^2}$$

By this time data were available for the primary and secondary ionization constants (k_1 and k_2) of hydrogen sulfide.

$$k_1{}^{[1]} = 0.91 \times 10^{-7}$$

$$k_2{}^{[2]} = 1.2 \times 10^{-15}$$

Therefore, if values for K_1 and K_2 could be determined experimentally, the solubility products of the corresponding sulfides could be obtained by multiplying these values by $k_1 \times k_2$. From the solubility products the molar solubilities are calculated in the usual way:

$$[Me_2S] = \sqrt[3]{\frac{L_{Me_2S}}{4}}, \quad \text{and} \quad [MeS] = \sqrt{L_{MeS}}$$

Bruner and Zawadzki undertook to measure the quantities necessary for the evaluation of K_1 and K_2 in a few typical cases. Selecting thallous sulfide (Tl_2S) as the first sulfide to study, because the precipitation of this sulfide was known to be a readily reversible process, equilibrium was reached in two ways: (1) by precipitation of neutral or slightly acid solutions of

[1] von Auerbach, *Z. physik. Ch.*, **49**, 220 (1904).
[2] Knox, *Z. Elektroch.*, **12**, 477 (1906); *Trans. Faraday Soc.*, **4**, 29 (1908).

thallous nitrate and sulfate with hydrogen sulfide; (2) by dissolving the thallous sulfide in sulfuric acid, either in a current of hydrogen sulfide (with constant concentration of the gas) or in closed tubes (with changing concentration of the gas). The solutions finally obtained were analyzed chemically to determine the concentrations of thallium, free acid, and hydrogen sulfide, and from these the concentrations of thallous ion, hydrogen ion, and hydrogen sulfide were calculated.

It is not worth while to describe or discuss the methods of analysis used. Available conductance data were used to calculate the extents of dissociation of the salt and of the acid present, assuming that in a mixture of two electrolytes having a common ion the extent of dissociation of each electrolyte will be that which the electrolyte would have if its concentration were equal to the sum of the concentrations of the two electrolytes. The summary of this first study is given in Table 23. Bruner and Zawadzki con-

TABLE 23

VALUES OF K_1 FOR Tl_2S

Series	No. of Expts.	Values of K_1		
		Max.	Min.	Average
1	12	0.581	0.463	0.522
2	6	.612	.572	.585
3	4	.759	.633	.711
4	7	.583	.493	.543

sidered the values in series 1 to be too low due to the method employed in estimating the acidity of the final solution. Series 2 and 4 involved thallous sulfate and sulfuric acid while series 3 involved thallous nitrate and nitric acid; so the single value for K_1, 0.637, to represent thallous sulfide, was derived from series 3 and the mean of series 2 and 4. From this value the solubility product is calculated by multiplying by $k_1 \times k_2$ or 1.092×10^{-22}, giving

$$L_{Tl_2S} = 7.0 \times 10^{-23}$$

Similar studies were undertaken for ferrous, cadmium and lead sulfides. For the first of these the selected value of K_2 was derived from two sets of experiments: (1) the precipitation with hydrogen sulfide from Mohr's salt ($FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$), and (2) the dissolving of ferrous sulfide in acetic acid in a current of hydrogen sulfide. In the case of cadmium sulfide dissolving experiments were carried out in approximately molar sulfuric acid containing a low concentration of hydrogen sulfide. Also precipitation experiments were carried out by letting cadmium sulfate and

hydrogen sulfide water stand for a fairly long time in a closed tube, then opening the tube and analyzing the resulting solution. Experiments were also carried out using cadmium chloride instead of cadmium sulfate. For lead sulfide only dissolving experiments with hydrochloric acid were tried.

Following the completion of these experiments older data in the literature for other sulfides were recalculated and the results expressed in a table along with those determined directly.

TABLE 24

EQUILIBRIUM CONSTANTS AND SOLUBILITY PRODUCTS OF THE METAL SULFIDES, ACCORDING TO BRUNER AND ZAWADZKI

Sulfide	K	L	Metal ion concn. if $[H^+] = 1$ and $[H_2S] = 0.1$	Molar solubility of sulfide	Observer
MnS........	6.3×10^{6}	7.0×10^{-16}		2.6×10^{-8}	Bruner-Zawadzki
FeS........	3.4×10^{3}	3.7×10^{-19}	3.4×10^{2}	6.1×10^{-10}	" "
Tl_2S........	6.37×10^{-1}	7.0×10^{-23}	2.5×10^{0}	2.6×10^{-8}	" "
αZnS.......	7.3×10^{-4}	8.0×10^{-26}	7.3×10^{-3}	2.8×10^{-13}	Schaefer
αZnS.......	4.5×10^{-4}	5.0×10^{-26}	4.5×10^{-3}	2.2×10^{-13}	Glixelli
βZnS.......	Approx. 10^{-2}	1.1×10^{-24}	1.0×10^{-1}	1.05×10^{-12}	"
CdS*.......	6.5×10^{-6}	7.1×10^{-28}	6.5×10^{-5}	2.7×10^{-14}	Bruner-Zawadzki
CdS†	4.6×10^{-7}	5.1×10^{-29}	4.6×10^{-6}	7.1×10^{-15}	" "
PbS........	3.1×10^{-6}	3.4×10^{-28}	3.1×10^{-5}	1.8×10^{-14}	" "
Bi_2S_3	2.5×10^{-25}	3.2×10^{-91}	1.6×10^{-11}	3.1×10^{-19}	Bernfeld
CuS........	5.3×10^{-20}	5.9×10^{-42}	5.3×10^{-19}	2.4×10^{-21}	Immerwahr
CuS........	1.1×10^{-20}	1.2×10^{-42}	1.1×10^{-19}	1.1×10^{-21}	Knox
Ag_2S.......	4.4×10^{-31}	4.8×10^{-53}	2.1×10^{-15}	2.3×10^{-18}	Lucas
Ag_2S.......	1.35×10^{-28}	1.5×10^{-50}	3.7×10^{-14}	1.6×10^{-17}	Bernfeld
Ag_2S.......	3.6×10^{-28}	3.9×10^{-50}	6.0×10^{-14}	2.1×10^{-17}	Knox
HgS........	7.0×10^{-26}	7.7×10^{-48}	7.0×10^{-25}	2.8×10^{-24}	Immerwahr
HgS........	9.0×10^{-32}	1.0×10^{-53}	9.0×10^{-31}	3.2×10^{-27}	Knox

* From $CdCl_2$. † From $CdSO_4$.

As a check on the values obtained by direct experimental study of equilibria in sulfide precipitation, the authors tried the method of calculating the solubility products of the sulfides from (a), the heats of formation of the compounds, (b), the standard electrode potentials for the metals, and (c), the potential for sulfur to sulfide ion. The mathematical relation had been developed by Bodländer.[1] An error in the original calculation led to the writing of a note correcting the earlier mistake.[2] The formula used for the actual calculation reads

$$\frac{Q}{46,200} = E_a + E_k - 0.029 \log L$$

[1] Bodländer, *Z. physik. Ch.*, **27**, 55 (1898).
[2] Bruner and Zawadzki, *Z. anorg. allgem. Ch.*, **67**, 455 (1910).

in which Q is the heat of formation of the sulfide, E_a is the electrode potential of sulfur to molar sulfide ion, E_k is the electrode potential of the metal to its ion in molar concentration, and L is the solubility product of the compound. By assuming the value for the solubility product of thallous sulfide to be correctly determined in the above experimental work, this may be substituted in the formula, along with values for Q and for E_k as taken from the literature, and the value for E_a calculated. Conversely, using this value for E_a (+0.545 volt), values for the solubility products of the other sulfides may be calculated. A comparison of the values thus calculated with those given in the above table shows a reasonably close agreement of the two sets of figures. This may be taken as confirming the relative orders of magnitude of the values thus put forth and indicating concordance between the experimental methods of Bruner and Zawadzki and those employed by the other workers whose data were recalculated for the above table.

§37. If one now compares the results of Bruner and Zawadzki with those of Weigel it is evident that there is an extraordinary discrepancy between the two. They are not even of the same order of magnitude, and the figures of Weigel have a much narrower range than do the others. It will be worth while to examine the bases of the two studies in trying to account for the divergence.

In calculating the solubility of the sulfides from the experimental data, Weigel made two primary assumptions: first, that the conductance due to the water did not change, therefore the change in conductance could be taken as a direct measure of the amount of sulfide dissolved; second, that the sulfide underwent complete hydrolysis into hydroxide and hydrogen sulfide, so that the actual change in conductance was due to the introduction of metallic and hydroxyl ions in concentrations equivalent to the amount of sulfide dissolved. These assumptions made the calculation of solubility very simple. Thus in the case of the first sulfide reported by Weigel — the mineral, lead glance — the specific conductance of the distilled water was given as 1.116×10^{-6}, and that of the solution, 1.679×10^{-6}. The change in specific conductance, 0.567×10^{-6}, was then considered as that of a lead hydroxide solution whose molar concentration could be calculated by multiplying by 1000 and dividing by the molar conductance of lead hydroxide. Thus:

$$M = \frac{0.567 \times 10^{-6} \times 1000}{(2 \times 61.5) + (2 \times 174)} = 1.2 \times 10^{-6}$$

From this the molar solubility of the lead sulfide was taken to be 1.2×10^{-6}.

It is, of course, obvious that the two assumptions noted above are self-contradictory, and that the conductance of the water can be subtracted directly only in the case of a substance that does not change the concentra-

tion of the hydrogen or hydroxyl ions. For substances of moderate solubility the error due to failure to consider the change in conductance of the water may be negligible if the relative concentrations are such that the hydrogen and hydroxyl ions represent only a small fraction of the conductance of the solution. In the case of relatively insoluble substances this error becomes so large that such a simplifying assumption is no longer justified. In such cases the calculation of solubility from conductance data becomes a fairly complex matter.

Thus, the conductance of distilled water is usually much greater than it would be if it were due only to hydrogen and hydroxyl ions at equal concentrations ($0.8 \times 10^{-7}\,N$ at 18°). This is due to the presence of carbon dioxide, dissolved from the air, forming a dilute solution of carbonic acid which dissociates appreciably into hydrogen and bicarbonate ions. (The effect due to the dissociation of the bicarbonate ion may be shown to be negligible.) If the ionization constant of carbonic acid and the equivalent conductances of the various ions are known, it is possible to calculate the composition of this dilute solution of carbonic acid from the specific conductance of the solution. The following values for ionization constants and equivalent conductances at 18° are taken from Davies:[1]

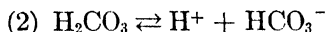
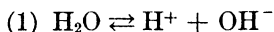
$$K_{H_2O} = [H^+] \times [OH^-] = 0.64 \times 10^{-14}$$

$$K_{1\,H_2CO_3} = \frac{[H^+] \times [HCO_3^-]}{[H_2CO_3]} = 3.12 \times 10^{-7}$$

Ion	H^+	OH^-	HCO_3^-
Equivalent conductance	316.6	176.6	40.1

Assuming that the main reactions will be

$$(1)\quad H_2O \rightleftarrows H^+ + OH^-$$

$$(2)\quad H_2CO_3 \rightleftarrows H^+ + HCO_3^-$$

the figure given by Weigel for the specific conductance of the distilled water in the above case (1.112×10^{-6}) may be considered equal to the sum of the specific conductances of the hydrogen, hydroxyl, and bicarbonate ions. From this the equation is set up:

$$1.112 \times 10^{-6} \times 1000 = 316.6\,[H^+] + 40.1\,[HCO_3^-] + 176.6\,[OH^-]$$

With the aid of the ionization constants given above, the concentrations of hydroxyl and bicarbonate ions may be expressed in terms of hydrogen ion,

[1] Davies, "The Conductivity of Solutions," John Wiley and Sons, Inc., New York, **1930**, pp. 52 and 181.

$$[H^+] = x$$

$$[OH^-] = \frac{0.64 \times 10^{-14}}{x}$$

$$[HCO_3^-] = x - \frac{0.64 \times 10^{-14}}{x} = [H^+] - [OH^-]$$

This value for $[HCO_3^-]$ is derived from the consideration that, as the H_2CO_3 dissociates, part of the H^+ is used to combine with OH^-, so the total quantity of H^+ supplied by the H_2CO_3 will equal the change in concentration of the H^+ plus the change in concentration of the OH^-. The concentration of HCO_3^- will be equal to the total quantity of H^+ supplied — neglecting secondary ionization of HCO_3^- — which is numerically equal to $[H^+] - [OH^-]$.

Substituting these expressions in the above equation:

$$1.112 \times 10^{-6} \times 1000 = 316.6x + 40.1\left(x - \frac{0.64 \times 10^{-14}}{x}\right) + 176.6\left(\frac{0.64 \times 10^{-14}}{x}\right)$$

This leads to a simplified equation,

$$x^2 - 3.118 \times 10^{-6}x + 0.245 \times 10^{-14} = 0$$

from which the following values are obtained:

$$[H^+] = 3.117 \times 10^{-6}$$
$$[OH^-] = 2.05 \times 10^{-9}$$
$$[HCO_3^-] = 3.115 \times 10^{-6}$$
$$[H_2CO_3] = 3.112 \times 10^{-5}$$
$$[HCO_3^-] + [H_2CO_3] = (\text{total carbonic acid in soln.}) = 3.423 \times 10^{-5}$$

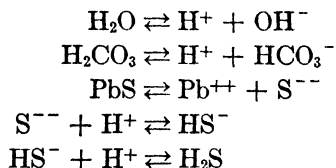
This represents the distilled water to which the lead sulfide was added. In order to use the conductance of the saturated solution to calculate the concentrations of the various ions to which the conductance was due, it is necessary to make certain additional assumptions.

1. Lead sulfide will undergo essentially complete hydrolysis.
2. Lead hydroxide is a strong enough base so there will be negligible combining of hydroxyl ion with lead ion in the very dilute solution obtained.[1]
3. Sulfide ion will react with hydrogen ion to such an extent as to leave a negligible concentration of sulfide ion in the solution, the relative amounts

[1] It is recognized that this assumption is contrary to fact, if the usual values for the ionization of lead hydroxide are accepted, but if this further reaction is added the problem becomes insoluble with the number of known quantities given. Therefore this assumption is necessary to permit the problem to be solved.

of bisulfide ion and of hydrogen sulfide formed being determined by the primary ionization constant of hydrogen sulfide.

4. The significant reactions occurring in the solution were:

$$H_2O \rightleftarrows H^+ + OH^-$$
$$H_2CO_3 \rightleftarrows H^+ + HCO_3^-$$
$$PbS \rightleftarrows Pb^{++} + S^{--}$$
$$S^{--} + H^+ \rightleftarrows HS^-$$
$$HS^- + H^+ \rightleftarrows H_2S$$

On the basis of the above assumptions the five ions to which the conductance of the solution was due are hydrogen, hydroxyl, bicarbonate, bisulfide and lead ions. Since the specific conductance of the saturated solution was 1.679×10^{-6} the equation may be set up of the same type as above, using as equivalent conductance for lead and bisulfide ions 60.5 and 62 respectively:

$$1.679 \times 10^{-6} \times 1000 = 316.6\,[H^+] + 176.6\,[OH^-] + 40.1\,[HCO_3^-] + 62\,[HS^-] + (2 \times 60.5)\,[Pb^{++}]$$

In addition to the ionization constants given before, the constant for the primary ionization of hydrogen sulfide will be needed for a solution of this equation.

$$K_{1\,H_2S} = \frac{[H^+] \times [HS^-]}{[H_2S]} = 0.9 \times 10^{-7}$$

With the aid of these and with the figures for the composition of the distilled water in which the lead sulfide was dissolved, the concentrations of the other ions may be expressed in terms of hydrogen ion as follows:

$$[H^+] = x$$

$$[OH^-] = \frac{0.64 \times 10^{-14}}{x}$$

$$[HCO_3^-] = 3.423 \times 10^{-5}\left(\frac{3.12 \times 10^{-7}}{3.12 \times 10^{-7} + x}\right)$$

$$[HS^-] = \frac{0.9 \times 10^{-7}\left(\dfrac{-x^3 - 3.07 \times 10^{-7}x^2 + 107 \times 10^{-13}x + 2.0 \times 10^{-21}}{3.12 \times 10^{-7}x + x^2}\right)}{0.9 \times 10^{-7} + 2x}$$

$$[Pb^{++}] = \frac{(0.9 \times 10^{-7} + x)\left(\dfrac{-x^3 - 3.07 \times 10^{-7}x^2 + 107 \times 10^{-13}x + 2.0 \times 10^{-21}}{3.12 \times 10^{-7}x + x^2}\right)}{0.9 \times 10^{-7} + 2x}$$

(The derivations of the expressions for the concentrations of the last 3 ions are given in some detail for the benefit of the student who has had little occasion to perform such tasks.)

1. The value for $[HCO_3^-]$ is derived as follows:

The total concentration of H_2CO_3 (molecular and ionized) was given above as 3.423 $\times 10^{-5}$

$$[HCO_3^-] = 3.423 \times 10^{-5} \times \text{(extent of dissociation of the } H_2CO_3)$$

$$\text{The extent of dissociation of } H_2CO_3 = \frac{[HCO_3^-]}{[HCO_3^-] + [H_2CO_3] \text{ (molecular)}}$$

If $\frac{[H^+] \times [HCO_3^-]}{[H_2CO_3]} = 3.12 \times 10^{-7}$, and $[H^+] = x$, $\frac{[HCO_3^-]}{[H_2CO_3]} = \frac{3.12 \times 10^{-7}}{x}$

and
$$\frac{[HCO_3^-]}{[HCO_3^-] + [H_2CO_3]} = \frac{3.12 \times 10^{-7}}{3.12 \times 10^{-7} + x}$$

Substituting 3.423×10^{-5} for the expression, $[HCO_3^-] + [H_2CO_3]$, and rearranging,

$$[HCO_3^-] = 3.423 \times 10^{-5}\left(\frac{3.12 \times 10^{-7}}{3.12 \times 10^{-7} + x}\right)$$

2. The value for $[HS^-]$ is derived as follows:

According to the equations for the significant reactions, there will be 1 hydrogen ion used for every bisulfide ion formed, and there will be 2 hydrogen ions used for every molecule of hydrogen sulfide formed. Therefore the total amount of hydrogen ion used will be $[HS^-] + 2\,[H_2S]$.

If $\frac{[H^+] \times [HS^-]}{[H_2S]} = 0.9 \times 10^{-7}$, and $[H^+] = x$, $\frac{[HS^-]}{[H_2S]} = \frac{0.9 \times 10^{-7}}{x}$

from which,
$$\frac{[HS^-]}{[HS^-] + 2\,[H_2S]} = \frac{0.9 \times 10^{-7}}{0.9 \times 10^{-7} + 2x}$$

Since $[HS^-] + 2\,[H_2S]$ = total H^+ used,

$$[HS^-] = \frac{(0.9 \times 10^{-7})\text{ (total } H^+ \text{ used)}}{0.9 \times 10^{-7} + 2x}$$

The total hydrogen ion used is derived from three sources:

(a) The direct change in $[H^+] = 3.117 \times 10^{-6} - x$.

(b) The decrease in $[H_2CO_3]$. The lowering of $[H^+]$ causes further dissociation of the carbonic acid, supplying hydrogen ion which is also used in the reaction. The new $[H_2CO_3]$ will be the total concentration of carbonic acid (molecular plus ionized) minus the new $[HCO_3^-]$. The total concentration of carbonic acid was given above as 3.423×10^{-5}, and the expression for the new $[HCO_3^-]$ is

$$3.423 \times 10^{-5}\left(\frac{3.12 \times 10^{-7}}{3.12 \times 10^{-7} + x}\right)$$

therefore the new value for

$$[H_2CO_3] = 3.423 \times 10^{-5} - 3.423 \times 10^{-5}\left(\frac{3.12 \times 10^{-7}}{3.12 \times 10^{-7} + x}\right)$$

which simplifies to $\frac{3.423 \times 10^{-5}x}{3.12 \times 10^{-7} + x}$.

The change in $[H_2CO_3]$ will be the original $[H_2CO_3]$ minus the new $[H_2CO_3]$, or,

$$3.112 \times 10^{-5} - \left(\frac{3.423 \times 10^{-5}x}{3.12 \times 10^{-7} + x}\right)$$

(c) The decrease in $[H_2O]$. As the $[H^+]$ is lowered there will be further dissociation of water, supplying additional hydrogen ion which is used in the reaction. Since 1 hydroxyl ion will be introduced for each molecule of water that dissociates, the decrease in $[H_2O]$ will be equal to the increase in $[OH^-]$. The latter will be the difference between the new and the original $[OH^-]$ or,

$$\frac{0.64 \times 10^{-14}}{x} - 2.05 \times 10^{-9}$$

The total hydrogen ion used will be the sum of these three quantities:

$$(3.117 \times 10^{-6} - x) + \left(3.112 \times 10^{-5} - \frac{3.423 \times 10^{-5}x}{3.12 \times 10^{-7} + x}\right) + \left(\frac{0.64 \times 10^{-14}}{x} - 2.05 \times 10^{-9}\right)$$

This simplifies to the form

$$\frac{-x^3 - 3.07 \times 10^{-7}x^2 + 107 \times 10^{-13}x + 2.0 \times 10^{-21}}{3.12 \times 10^{-7}x + x^2} = \text{total H}^+ \text{ used}$$

Substituting this in the earlier equation, the expression is obtained for $[HS^-]$.

3. The value for $[Pb^{++}]$ is derived as follows: for every molecule of lead sulfide that dissociates there will be 1 lead ion and 1 sulfide ion produced. If the sulfide ions react practically completely to form bisulfide ion and hydrogen sulfide, the concentration of lead ion accumulating in the solution will equal the sum of the concentrations of bisulfide ion and hydrogen sulfide:

$$[Pb^{++}] = [HS^-] + [H_2S]$$

If $\frac{[H^+] \times [HS^-]}{[H_2S]} = 0.9 \times 10^{-7}$, and $[H^+] = x$, $\frac{[H_2S]}{[HS^-]} = \frac{x}{0.9 \times 10^{-7}}$

and $\frac{[H_2S]}{[HS^-] + 2\,[H_2S]} = \frac{x}{0.9 \times 10^{-7} + 2x}$

Since $[HS^-] + 2\,[H_2S] =$ (total H^+ used), this may be substituted in the last equation, giving, after rearrangement,

$$[H_2S] = \frac{x\,(\text{total H}^+ \text{ used})}{0.9 \times 10^{-7} + 2x}$$

Therefore $[HS^-] + [H_2S] = \frac{(0.9 \times 10^{-7} + x)(\text{total H}^+ \text{ used})}{0.9 \times 10^{-7} + 2x} = [Pb^{++}]$

Substituting the expression derived above for (total H^+ used) the equation is obtained for $[Pb^{++}]$.

On putting the values thus derived into the equation,

$$1.679 \times 10^{-6} \times 1000 = 316.6\,[H^+] + 176.6\,[OH^-] + 40.1\,[HCO_3^-] + 62\,[HS^-] + (2 \times 60.5)[Pb^{++}]$$

and simplifying, the following equation is obtained:

$$x^4 - 6.22 \times 10^{-6}x^3 + 1.87 \times 10^{-12}x^2 + 3.95 \times 10^{-19}x + 12.6 \times 10^{-29} = 0$$

Solving this equation, $x = 4.51 \times 10^{-7}$. Using this value for the concentration of hydrogen ion in the saturated lead sulfide solution, the concentration of the other ions may be calculated from the equations given above. These calculations lead to those given in Table 25. If the concentration

TABLE 25

COMPOSITION OF A SATURATED SOLUTION OF LEAD SULFIDE AT 18°

Specific conductance of the solution = 1.679×10^{-6}
Specific conductance of the distilled water = 1.112×10^{-6}

$[H^+] = 4.51 \times 10^{-7}$
$[OH^-] = 1.42 \times 10^{-8}$
$[HCO_3^-] = 1.40 \times 10^{-5}$
$[HS^-] = 1.23 \times 10^{-6}$
$[Pb^{++}] = 7.405 \times 10^{-6}$

of lead ion is taken as representing the total solubility of the lead sulfide, this is found to be more than six times as great as that calculated by Weigel.

The work of Bruner and Zawadzki involved the determination of the solubility product of the sulfide, from which the solubility is calculated by a simple process (in the case of lead sulfide, extract the square root of the solubility product). It is possible to use the secondary ionization constant of hydrogen sulfide,

$$K_{HS^-} = \frac{[H^+] \times [S^{--}]}{[HS^-]} = 1.2 \times 10^{-15}$$

and calculate the solubility product of lead sulfide from the above data.

$$[S^{--}] = \frac{1.2 \times 10^{-15} \times [HS^-]}{[H^+]} = \frac{1.2 \times 10^{-15} \times 1.23 \times 10^{-6}}{4.51 \times 10^{-7}} = 3.27 \times 10^{-15}$$

$$L_{PbS} = [Pb^{++}] \times [S^{--}] = 7.40 \times 10^{-6} \times 3.27 \times 10^{-15} = 2.42 \times 10^{-20}$$

The square root of this figure is 1.55×10^{-10}, and may be considered to be the solubility lead sulfide would have if no hydrolysis or other secondary reaction occurred.

This, then, is the figure, derived by more accurate calculation from the work of Weigel, that should be compared with the solubility of lead sulfide obtained from the solubility product reported by Bruner and Zawadzki, reducing the ratio of the two from 6.5×10^{-7} (as shown in the literature) to 8.4×10^{-3}. In other words, this recalculation has brought the first value more than half way into line with the second one.

Similar recalculations of the data of Weigel for the three precipitated sulfides, lead sulfide, cadmium sulfide and manganous sulfide, are summarized in Table 26.

In considering these data it must be remembered that assumptions are involved in the calculations such that, while these figures are more significant than those reported by Weigel, they may still be considerably in error. Two of these assumptions may be outlined in some detail so as to make their importance clear.

TABLE 26

COMPOSITION OF SATURATED SOLUTIONS OF SULFIDES AS RECALCULATED FROM WEIGEL'S DATA

	PbS	CdS	MnS
Specific conductance of water	1.230×10^{-6}	1.206×10^{-6}	1.261×10^{-6}
Specific conductance of solution	2.922×10^{-6}	5.194×10^{-6}	32.6×10^{-6}
$[H^+]$	2.37×10^{-7}	0.40×10^{-7}	8.68×10^{-11}
$[OH^-]$	2.7×10^{-8}	1.59×10^{-7}	7.37×10^{-5}
$[HCO_3^-]$	2.38×10^{-5}	3.54×10^{-5}	4.35×10^{-5}
$[HS^-]$	3.77×10^{-6}	1.87×10^{-5}	1.17×10^{-4}
$[Me^{++}]$	1.37×10^{-5}	2.71×10^{-5}	1.17×10^{-4}
$[L_{MeS}]$	2.6×10^{-19}	15.2×10^{-18}	19×10^{-14}
$[S_{MeS}]$	5.0×10^{-10}	3.9×10^{-9}	4.36×10^{-7}

Case I. In the recalculation, as in Weigel's original calculations, it is assumed that the hydroxides are nearly enough completely ionized in the saturated aqueous solutions of the sulfides so that the combining of metallic ion with hydroxyl ion is of only negligible importance in the system. It has already been indicated that unless such an assumption is made the mathematical equation will contain too many unknowns to be solved from the data given. But it is obvious that many of these hydroxides are relatively weak bases and therefore the extent of dissociation will be far from complete even in fairly dilute solutions. Thus, for lead hydroxide, J. K. Wood[1] gives the value for the secondary basic ionization,

$$K_{2\,Pb(OH)_2} = \frac{[Pb^{++}]\,[OH^-]}{[PbOH^+]} = 3.09 \times 10^{-8}$$

Therefore
$$\frac{[Pb^{++}]}{[PbOH^+]} = \frac{3.09 \times 10^{-8}}{[OH^-]}$$

Inserting the value for the concentration of hydroxyl ion (1.42×10^{-8}) calculated for the saturated solution of the mineral lead glance, the concentration of $PbOH^+$ is found to be 46% that of the lead ion, so the total concentration of lead in the solution will be a considerable percentage higher than the concentration of lead ion. For precipitated lead sulfide, the data in Table 26 ($[OH^-] = 2.7 \times 10^{-8}$) show that the concentration of $PbOH^+$ will be 87% that of lead ion, so the error in the above assumption is hardly to be considered as negligible.

Case II. In the recalculation it is further assumed that the amount of carbon dioxide (plus its reaction products with water) remains constant

[1] Wood, *J. Ch. Soc.*, **97**, 889 (1910).

during the preparation of the saturated solution of the sulfide, and may be considered as accurately given by calculation from the specific conductance of the water. But, for a solution in equilibrium with air of definite carbon dioxide content there will be essentially constant concentration of molecular carbonic acid. For the distilled water used with the lead glance it was calculated above that the total carbonic acid in the solution was 3.423×10^{-5} M, the concentration of molecular carbonic acid being 3.112×10^{-5} M, and bicarbonate ion 3.115×10^{-6} M. Thus, assuming this solution to be in equilibrium with the air, at $[H^+] = 3.117 \times 10^{-6}$, the ratio of $[HCO_3^-]$ to $[H_2CO_3]$ was 0.11. But as the sulfide dissolved the solution became more alkaline, setting up a $[H^+]$ of approximately 4.51×10^{-7}. If exposure to the air was permitted and the concentration of carbon dioxide in the latter remained unchanged, the carbon dioxide would have dissolved until a ratio of $[HCO_3^-]$ to $[H_2CO_3]$ of approximately 0.78 was reached, so that if the concentration of molecular carbonic acid was considered to remain constant at 3.112×10^{-5} there would have been a very significant further absorption of carbon dioxide. In a similar way, calculation of the ratio of $[HCO_3^-]$ to $[H_2CO_3]$ for the saturated solutions reported in Table 26 for the precipitated sulfides of lead, cadmium and manganese shows values of 1.48, 8.75 and 401 respectively. It is recognized, of course, that in the final process of saturation the flasks were closed and therefore the effect being discussed would not reach equilibrium; but it is equally obvious that it would take place to a significant extent unless considerable care were taken to ensure the absence of carbon dioxide from the air that came in contact with the solution before the flask was closed for the final shaking, and, further, unless the flasks were closed tightly enough to prevent diffusion of carbon dioxide into the solution.

It will be noted that the effect of these errors in the assumptions made would be to cause the sulfides to dissolve to a still greater extent than is indicated by the concentrations of metallic ions shown in the above table. Therefore these values may be taken as indicating minimum figures for the solubilities of the sulfides in water. Other errors might well be mentioned (possible oxidation of sulfide ion, for instance), but these are sufficient to indicate the fact that even the recalculated figures have only approximate significance.

The figures for lead, cadmium and manganous sulfides given by Weigel, those recalculated from his data, and those by Bruner and Zawadzki, are set side by side in Table 27, and certain comparisons made. The points of chief interest in the table are (1) The sulfides dissolve to a greater extent in distilled water than even Weigel's figures indicate. This is shown by a comparison of data in columns 2 and 3 as indicated in column 6. (2) The error in Weigel's method of calculation increases as the solubility of the sulfide decreases. This is also shown in column 6. Thus, for manganous sulfide — the most soluble of the sulfides commonly precipitated in the

group separations of qualitative analysis — the solubility is at least 63% greater, while for the precipitated lead sulfide the solubility is at least 280% greater than calculated by Weigel. (3) The hypothetical solubilities as obtained from the solubility product principle are given in column 4 for Weigel's recalculated data, and in column 5 for Bruner and

TABLE 27

VARYING FIGURES FOR THREE SULFIDES

1	2	3	4	5	6
	S_{MeS} according to Weigel	$[Me^{++}]$ recalc. from Weigel's data	$\sqrt{L_{MeS}}$ recalc. from Weigel's data	$\sqrt{L_{MeS}}$ Bruner-Zawadzki	$\frac{[Me^{++}]}{S_{MeS}}$
PbS......	3.6×10^{-6}	1.37×10^{-5}	5.0×10^{-10}	1.8×10^{-14}	3.8
CdS..........	8.86×10^{-6}	2.71×10^{-5}	3.9×10^{-9}	2.7×10^{-14}	3.06
MnS..........	71.6×10^{-6}	11.7×10^{-5}	4.36×10^{-7}	2.6×10^{-8}	1.63
Ratio $\frac{CdS}{PbS}$....	2.2	1.9	7.8	1.3	
Ratio $\frac{MnS}{PbS}$....	19.9	8.5	8.7×10^{2}	1.4×10^{6}	

Zawadzki's data. On comparison of the figures of column 4 with those of column 2 it will be seen that there is a much greater range of difference shown in the former than in the latter. Line 5, column 2, shows manganous sulfide as being only 19.9 times as soluble as lead sulfide (in column 3 it appears only 8.5 times as soluble), while column 4 shows it to be 870 times as soluble if the effect of hydrolysis of sulfide ion is eliminated. One of the chief arguments against the accuracy of Weigel's figures has been the inability to account for the usual analytical separations among the sulfides in terms of the varying solubilities of the different compounds. The increased range shown in column 4 is a step in the right direction. The figures in column 5 show a still greater range, due to the enormous difference in solubilities shown at the extremes. Thus for manganous sulfide the figure in column 4 is only 16.8 times that in column 5, while for lead sulfide it is nearly 28,000 times as great. The simplicity of the explanation of the analytical separations with the use of the figures by Bruner and Zawadzki has undoubtedly lead to uncritical acceptance of them. It is interesting to note, however, that in the cases of cadmium and lead sulfides the differences in column 4 are greater than those in column 5, the ratios being given in line 4. If the figures given by Bruner and Zawadzki for cadmium sulfide from cadmium sulfate ($L_{CdS} = 5.1 \times 10^{-29}$), instead of those from cadmium chloride, were taken the apparent solubility relations of the two sulfides would be even more divergent from those in column 4; the ratio $\frac{\sqrt{L_{CdS}}}{\sqrt{L_{PbS}}}$ becoming 0.39 instead of 1.3. The obvious

explanation of this lies in the well-known capacity of chloride ion to combine with cadmium ion with formation of a complex ion, so that only a moderate fraction of the cadmium would be present in the form of the simple ion. This would lead to too high a value for the solubility product of the cadmium sulfide if it were assumed that the cadmium were all present as cadmium ion. Undoubtedly a similar discrepancy would have been observed in the case of lead if experiments had been carried out with other than lead chloride and hydrochloric acid solutions. Since the disturbing influence of the chloride ion was not present in Weigel's experimental work it is probable that the figures recalculated from his data represent the relative solubilities of cadmium and lead sulfides with respect to each other more accurately than do those of Bruner and Zawadzki.

Finally, in considering these two pieces of work, the question may be asked, which set of figures is the more nearly correct? No categorical answer can be given. It depends on what the figures are to be used for. If one is washing a sulfide with distilled water and wishes to know how much can be used before the solubility loss becomes significant, the values of Weigel are much nearer the truth than those of Bruner and Zawadzki. But if one wishes to calculate the probable accuracy of a separation in the presence of a certain concentration of hydrogen ion, the situation is just reversed. The main difference between the two is that to the hypothetical solubility of the sulfides (the solubility if no side reactions, hydrolysis, etc. occurred) Weigel adds the solubility due to hydrolysis, while Bruner and Zawadzki add such solubilities as may be due to the presence of relatively high concentrations of accessory ions, such as chloride, sulfate, etc.

In passing, it may be noted that the chief argument against the extremely low figures given by Bruner and Zawadzki for the less soluble sulfides lies in the moderate rapidity of reactions involving the dissolving or formation of the precipitates, as contrasted with the low rates that would be expected if the concentrations of the reacting ions were as low as the calculations would seem to indicate. Since slightly soluble compounds show specific differences in rates of precipitation and of dissolving, these factors must be taken into account as well as the solubilities of the different compounds in explaining the separations obtained. On that basis it is not necessary to have the extreme range of solubilities suggested in the figures of Bruner and Zawadzki in order to explain the analytical separations in use.

§38. The next set of solubility determinations that will be discussed is the work of Remy and Kuhlmann.[1] The pure oxides of magnesium, beryllium, aluminum, zinc, cadmium, lead, copper and silver were prepared by recrystallizing the corresponding nitrates, precipitating the hydroxides with freshly distilled ammonium hydroxide — sometimes dissolving this precipitate in nitric acid and reprecipitating with ammonium

[1] Remy and Kuhlmann, *Z. anal. Ch.*, **65**, 1–24, 161–81 (1924–5).

hydroxide — and finally heating strongly in a porcelain crucible. In the case of silver oxide care was taken to avoid decomposition by excessive heat. The case of magnesium oxide, the most soluble one in the list, was then taken up in detail and experimental studies carried out from which procedures were developed that were then applied to the other compounds.

In studying magnesium oxide, the freshly ignited (and only slightly cooled) oxide was transferred to a flask containing distilled water, the stopper of the flask inserted and the mixture shaken for 4 hours to prepare the saturated solution. The solution was filtered, the first portion being discarded, and 200 cc. of the filtrate evaporated in a platinum dish and ignited. In four experiments the residues obtained were 3.5, 3.4, 3.4, and 3.5 mg. On repeating the determination using conductance water ($\gamma = 1 \times 10^{-6}$) instead of the usual redistilled water ($\gamma = 4 \times 10^{-6}$), appreciably lower values were obtained due to the presence of less carbonic acid to react with the magnesium hydroxide. Using the latter figure, 3.2 mg. of magnesium oxide in 200 cc. of water, the solubility of magnesium oxide (or hydroxide) is calculated to be 3.97×10^{-4} moles per liter.

Considering this figure as standard, the saturated solutions were next subjected to conductance measurements. Portions of the solution were filtered after 24, 48, and 72 hours contact with the solid. The specific conductances, after subtracting the value for the water used, were as follows:

Specific Conductance

Time elapsed, hrs.	1st sample	2nd sample	3rd sample
24	9.613×10^{-5}	9.799×10^{-5}	9.353×10^{-5}
48	8.751×10^{-5}	8.725×10^{-5}	
72	8.271×10^{-5}	8.328×10^{-5}	

It was noted that the conductance of the saturated solution decreased on standing. On evaporating 200 cc. portions of the final solution to dryness residues were obtained of 3.6 and 3.5 mg., somewhat more than the 3.2 mg. found above with conductance water, but checking the results with the redistilled water. As an obvious explanation for the decrease in conductance, it was suggested that carbon dioxide was being absorbed from the air and that a reaction took place between this and hydroxyl ion in the solution, $CO_2 + 2\,OH^- = CO_3^{--} + H_2O$, thus replacing an ion of high mobility with one of lower mobility. Calculations showed that even for the conductance water used this would produce a decrease in specific conductance of 0.44×10^{-5} reciprocal ohms. Therefore such a correction, based on calculation of the carbon dioxide content of the water used, should be added to the specific conductance of the solution, instead of subtracting a water correction as in the usual procedure.

Starting fresh experiments in which the saturation was carried out in a glass stoppered conductance cell and measurements of resistance were made from time to time, it was found that the minimum resistance was obtained in approximately $3\frac{3}{4}$ hours. It was considered, therefore, that saturation was complete by the end of this time and in later experiments the shaking was continued at least this long. Three determinations gave specific conductances respectively of 15.17×10^{-5}, 14.56×10^{-5} and 14.80×10^{-5} reciprocal ohms (the correction for carbonic acid in the conductance water having been added as indicated above). From these the solubilities were calculated by the usual formula, the average of the three being 3.48×10^{-4} moles per liter.[1]

Following this, attention was turned to the possibility of measuring the solubility of the hydroxide by still a third method; namely, by conductometric titration of the saturated solution with dilute acid. This method involved principally the fact that the mobilities of hydrogen and of hydroxyl ion are relatively high, so that as dilute acid was added in small amounts at a time the conductance of the solution would decrease to a fairly marked extent until the solution became neutral, following which the addition of more acid would cause a sharp increase in conductance. By using a definite volume of solution and plotting the volume of standard acid used against the resistance (or conductance) of the solution the point of inflection of the resistance could be determined. The amount of standard acid required to reach this point would be a measure of the amount of alkali neutralized. From this the concentration of the solution could be calculated, and if the solution was saturated with respect to a particular hydroxide, this would be the solubility of that compound.

Preliminary studies with dilute, known mixtures of potassium hydroxide and sodium carbonate using 0.01 *N* hydrochloric acid gave fairly sharp end-points. The accuracy of the end-point was still further improved by adding a measured excess of the acid, boiling out the carbon dioxide, and titrating the free acid with standard alkali.

[1] In comparing this value with the one obtained by direct gravimetric procedure (3.97×10^{-4} moles per liter) attention was called to the fact that a systematic error was involved in the lower value which should make it lower than the other, in that no account was taken of the amount of carbon dioxide that diffused into the solution during the time of saturating. It happens, however, that Remy and Kuhlmann gave some data from which this effect might be evaluated, although they failed to make use of it. Thus in the third of the above determinations the increase in resistance was measured at intervals for an hour beyond the regular $3\frac{3}{4}$ hours. Following the usual practice for determinations of this type, in which a correction is to be applied for a systematic error, it may be assumed that carbon dioxide was being absorbed at a uniform rate during the whole time of the experiment. On this basis, the increase in resistance during the hour following saturation, multiplied by $3\frac{3}{4}$, gives a correction to be subtracted from the resistance noted at the end of $3\frac{3}{4}$ hours in order to obtain the resistance that would characterize the magnesium hydroxide solution if no further carbon dioxide had been absorbed. On applying this correction to the data of the third determination, the solubility of magnesium hydroxide is calculated to be 4.16×10^{-4} moles per liter, distinctly closer to the value obtained gravimetrically than the one obtained without this correction.

On applying the procedure to saturated magnesium hydroxide solutions, and using sulfuric acid instead of hydrochloric acid to avoid possible loss during the boiling, the average of three concordant determinations gave the solubility of magnesium hydroxide as 3.92×10^{-4} moles per liter. This number checks very closely with the value obtained by the gravimetric method, and is only slightly lower than the recalculated figure obtained from the conductance data.

In turning to the study of other less soluble oxides, Remy and Kuhlmann used both the conductance of the saturated solution and the conductometric titration of the solution to obtain data for calculating solubilities. The results are summarized in Table 28. In considering these data it should

TABLE 28

SOLUBILITY DETERMINATIONS BY REMY AND KUHLMANN

Oxide	Time for prepn. of satd. soln., hrs.	Specific conductance of soln. $\times 10^5$	Conductance Data		Conductometric Data			
			Correction for CO_2 in water $\times 10^5$	Solv. $M \times 10^5$	Vol. titrated, cc.	Concn. of acid, N	of acid used, cc.	Solv. $M \times 10^5$
MgO	$3\frac{1}{4}$	14.36	+0 44	34.8	80	0 01	6.27	39.2
Al_2O_3	5	1 056	.250	1.02	"	.001	4.40	0.92
ZnO	1	1.392	264	3.76	"	"	5 73	3.58
CdO	$1\frac{1}{2}$	1.441	.269	3.90	"	"	5.98	3.74
PbO	1	2.293.	.280	5 52	"	.002	4.44	5.55
CuO	3	2.668	.282	6 77	"	"	5.49	6.86
Ag_2O	1	4.520	.308	10.7	"	005	3.49	10.9
BeO	$1\frac{1}{2}$	.1729	.156	.81	The solution was too dilute to give results by this method.			

be remembered that further absorption of carbon dioxide during the time required for saturation would tend to raise the solubility still more, though only in the cases of aluminum and copper oxides was the time required of the same order as for magnesium oxide, where the conductance data made it possible to calculate the corresponding correction. Further, in the conductometric titration the amount of acid used would correspond to the sum of the hydroxyl, carbonate and bicarbonate concentrations plus any potential source of these materials, such as molecular or colloidal magnesium hydroxide, etc. The significance of this may be considered after the next paper has been discussed in which another method was used to determine the solubilities of various of the hydroxides.

§39. In 1925, Britton[1] published a series of electrometric studies on the precipitation of hydroxides. By preparing salt solutions of known concentration and determining the concentration of hydroxyl ion at which precipitation of the hydroxide first appears, data are available from which the solubility products of the hydroxides may be calculated. The difficulty is to measure the concentration of hydroxyl ion in the solution. In Britton's work this was done indirectly by measuring the electrode potential of a hydrogen electrode in the solutions, calculating the concentration of hydrogen ion corresponding to the measured potential, and finally calculating the concentration of hydroxyl ion corresponding to that concentration of hydrogen ion.

A hydrogen electrode consists of platinum foil, coated with platinum black and saturated with hydrogen, the latter supplied by bubbling the gas through the solution at a moderate rate. Under standard conditions (such as fixed temperature, fixed pressure of hydrogen and fixed concentration of hydrogen ion in the solution in contact with the electrode) this electrode possesses a definite potential. This potential can be measured by comparison with a standard electrode whose potential is arbitrarily set at some definite value. By measuring the potential difference between the two electrodes when they are joined into a cell, a number is obtained which may be added to or subtracted from the assumed potential of the standard electrode (according to whether the electrode in question is positive or negative as compared with the standard electrode), to obtain the potential of the electrode in question. The standard electrode used by Britton was a "normal calomel electrode." This is an electrode of mercury, covered with a solution that contains both mercurous chloride and potassium chloride, the solution being saturated with respect to the former compound and of *N* concentration with respect to the latter. Such an electrode, on the hydrogen scale, has a potential of +0.283 volt at 18°. On comparing this with a hydrogen electrode at 18°, with the hydrogen at standard pressure and with the concentration of hydrogen ion in the solution exactly *N*, a potential difference of 0.283 volt is observed. Since the hydrogen electrode is negative as compared with the normal calomel electrode, this quantity is subtracted from the potential of the normal calomel electrode to obtain the potential of the hydrogen electrode: $0.283 - 0.283 = 0$. However, if the concentration of hydrogen ion in the solution bathing the hydrogen electrode is other than normal the difference in potential of the 2 electrodes will not be 0.283 volt, but greater or less than this according to whether the concentration of hydrogen ion is less than or greater than normal. Thus the potential of a hydrogen electrode varies according to the concentration of hydrogen ion in the solution, and the measured potential may be used as a basis for calculating the concentration of hydrogen ion in a particular solution. From theoretical considerations and by actual experiment (with side interferences eliminated) the potential of a hydrogen electrode is found to change 0.058 volt (at 18°) for every tenfold change in concentration of hydrogen ion in the solution. Thus if a hydrogen electrode were in contact with a solution of 0.1 *N* hydrogen-ion concentration its potential would be −0.058. That is, the difference in potential of this electrode and a normal calomel electrode would be 0.341 volt. The mathematical formulas used to show the relation of the concentration of hydrogen ion to the potential of the hydrogen electrode, and the relation of the concentration of hydrogen ion to the difference in potential of the hydrogen and normal calomel electrodes, are

$$(1)\quad E_{H_2} = 0.058 \log [H^+]$$

$$(2)\quad \frac{\text{E.M.F.} - 0.283}{0.058} = \log \frac{1}{[H^+]} = -\log [H^+]$$

[1] Britton, *J. Ch. Soc.*, **127**, 2110–2159 (1925).

Applying this to the problem under consideration; it was found experimentally that when 100 cc. of 0.025 M $MgSO_4$ solution was treated with 0.099 N NaOH solution until precipitation became barely visible the difference in potential of a normal calomel electrode and a hydrogen electrode dipping into this solution was 0.885 volt. From this,

$$\log \frac{1}{[H^+]} = \frac{0.885 - 0.283}{0.058} = 10.38$$

and

$$[H^+] = \frac{1}{10^{10.38}} = 1 \times 10^{-10.38}$$

To convert this last figure into the more common form it is necessary to refer to a table of logarithms. Thus, the number $1 \times 10^{-10.38}$ is the same as $(1 \times 10^{-10})(1 \times 10^{-0.38})$, which in turn is equal to $(1 \times 10^{-11})(1 \times 10^{0.62})$; 0.62 is the logarithm of the number, 4.17; therefore $1 \times 10^{-10.38} = 4.17 \times 10^{-11}$.

In this connection it should be noted that the symbol pH is commonly substituted for the expression $\log \frac{1}{[H^+]}$ in the above equation. Much of the literature of chemistry today discusses the acidity or alkalinity of a solution in terms of pH. Thus in the paper now under discussion the tables give columns headed pH instead of $[H^+]$, the pH at which magnesium hydroxide began to precipitate being 10.38. Since $\log \frac{1}{[H^+]} = -\log [H^+]$, the concentration of hydrogen ion may be written $[H^+] = 1 \times 10^{-pH}$. Such a number is obtainable very simply from the experimental data, it can be used for calculations as easily as any of the other forms for expressing the concentration of hydrogen ion in the solution, and may be converted to the other forms when desired with the aid of a table of logarithms.

Since it is difficult to judge the exact point at which precipitation starts, it was found advantageous to plot the curves for change of E.M.F. as the sodium hydroxide was added, and then extend the straight portions of the lines adjacent to the sharp part of the curves, using the intersection points to indicate the E.M.F. and the amount of sodium hydroxide added for initial precipitation. On doing this with the data for the magnesium sulfate solution the following figures were obtained:

E.M.F. at initial pptn.	0.892
Cc. of 0.099 N NaOH added	0.5
pH for initial pptn.	10.50

The concentration of hydroxyl ion in the solution was calculated by the use of the water constant, K_w.

$$K_w = 0.73 \times 10^{-14} \text{ at } 18°$$

$$[OH^-] = \frac{0.73 \times 10^{-14}}{[H^+]}$$

since

$$0.73 \times 10^{-14} = 1 \times 10^{-14.14}$$

$$pOH = 14.14 - pH$$

Substituting the value of pH given above,

$$pOH = 14.14 - 10.50 = 3.64$$

$$[OH^-] = 1 \times 10^{-3.64} = 2.3 \times 10^{-4}$$

The concentration of metallic ion in the solution was calculated from the following data and assumptions:

(a) the concentration of the salt solution used,
(b) the volume of the solution taken,
(c) the concentration of the sodium hydroxide solution used,
(d) the volume of the sodium hydroxide solution added,
(e) the salt was assumed to be completely ionized, with no intermediate ions present,
(f) the hydroxyl ion added was assumed to produce an equivalent lowering in concentration of metallic ion.

Thus, in adding to 100 cc. of 0.025 *M* magnesium sulfate solution 0.5 cc. of 0.099 *N* sodium hydroxide solution, the concentration of magnesium ion would be considered as reduced from 0.025 *M* to 0.0248 *M* through the combining of magnesium ion with hydroxyl ion, and still further to 0.0246 *M* by reason of dilution of the solution from 100 cc. to 100.5 cc.[1]

In discussing the hydrogen electrode Britton called attention to the fact that it cannot be used in the presence of metals below hydrogen in the electromotive series, nor with ferric salts, and that it showed abnormal behavior with lead and cadmium salts. For these metals it was found possible to use an oxygen electrode, converting the voltages of the oxygen electrode-normal calomel electrode cell into pH values by starting with a solution containing sufficient free acid so that its pH was known and titrating to a sufficient excess of alkali so that the final pH could be considered

[1] In the original paper an oversight in calculation led to substituting the amount that the concentration of metallic ion was reduced by the sodium hydroxide for the concentration of metallic ion assumed in the solution. Thus $[Mg^{++}]$ was put at 2.5×10^{-4} instead of $(0.025 - 2.5 \times 10^{-4}) \frac{100}{100.5}$. This caused the calculated values for the solubility products of the hydroxides to be considerably lower than the experimental data would actually warrant. In Table 29 the concentrations of metallic ions are recalculated instead of taken from Britton's tables.

as known. The intermediate pH's were then calculated by simple proportion.

In Table 29 the data of the more common of the hydroxides covered by Britton have been assembled and the solubility products and solubilities calculated. Britton noted that the method used to calculate solubility products was open to the objections (a) the difficulty of estimating accurately the amount of alkali required to produce initial precipitation, and (b) the fact that basic salts were actually precipitated which may have had some effect on both the hydroxyl and the metal-ion concentrations.

TABLE 29

SOLUBILITY PRODUCTS OF METALLIC HYDROXIDES ACCORDING TO BRITTON

pH	Solution studied	$[M^{++}]$*	$[OH^-]$	L	S
10.50	0.025 M $MgSO_4$	0.0246	2.3×10^{-4}	1.3×10^{-9}	6.9×10^{-4}
8.81	.024 M $MnCl_2$	.0233	4.7×10^{-6}	5.1×10^{-13}	5.0×10^{-5}
6.84	.0247 M $CoCl_2$	.0240	5.0×10^{-8}	6.0×10^{-17}	2.5×10^{-6}
6.76	.025 M $NiCl_2$	.0244	3.3×10^{-8}	2.7×10^{-17}	1.9×10^{-6}
5.72	.025 M $FeSO_4$	.0246	3.8×10^{-9}	3.6×10^{-19}	4.2×10^{-9}
4.10	.00677 M $Al_2(SO_4)_3$	.0113	9.1×10^{-11}	8.5×10^{-33}	4.2×10^{-9}
5.64	.02 M $BeSO_4$	.00786	3.2×10^{-9}	8.0×10^{-20}	2.8×10^{-7}
5.17	.025 M $ZnSO_4$	.0246	1.1×10^{-9}	3.0×10^{-20}	2.0×10^{-7}
5.31	.01 M $KCr(SO_4)_2$	.0061	1.7×10^{-9}	2.9×10^{-29}	3.2×10^{-8}
1.84	.02 M $SnCl_2$	....	....	....	....
2.78	.01 M HCl	.00496 (opalescent)	5.0×10^{-13}	3.1×10^{-52}	....
	.01 M $ZrCl_4$	.00123 (ppt.)	4.4×10^{-12}	4.5×10^{-49}	
7.4	.0212 N HCl .02 M $HgCl_2$	.016	1.8×10^{-7}	5.2×10^{-16}	5.1×10^{-6}
6.7	.0199 N H_2SO_4 .02 M $CdSO_4$	.017	3.6×10^{-8}	2.2×10^{-17}	1.8×10^{-6}
6.0	.0202 N HNO_3 .02 M $Pb(NO_3)_2$	.016	7.2×10^{-9}	8.3×10^{-19}	5.9×10^{-7}
5.7	.0202 N HNO_3 .04 M $AgNO_3$	.033	3.6×10^{-9}	1.2×10^{-10}	1.1×10^{-5}(?)
5.5	.0199 N H_2SO_4 .02 M $CuSO_4$	.016	2.3×10^{-9}	8.5×10^{-20}	2.8×10^{-7}
4.2	.0149 N HNO_3 .00833 M $U(NO_3)_6$	.00097	1.1×10^{-10}	1.7×10^{-63}	....
2.3	.0202 N HCl .0133 M $FeCl_3$	.0047	1.4×10^{-12}	1.3×10^{-38}	1.5×10^{-10}

* The values for $[M^{++}]$ were recalculated from the experimental data instead of taken from Britton's tables (see footnote, p. 120).

§40. On comparing the results of Britton with those of Remy and Kuhlmann on the solubilities of the same hydroxides, differences will be

noted somewhat similar in character to those in the two articles on the sulfides by Bruner and Zawadzki and by Weigel, respectively. The values reported by Britton are distinctly lower than those of Remy and Kuhlmann (except in the case of $Mg(OH)_2$ where the solubility calculated from Britton's data is 6.9×10^{-4} while that from the conductometric titration by Remy and Kuhlmann is 3.9×10^{-4}). Further, there is a much wider range in the figures of Britton than in the others; the latter giving magnesium hydroxide a solubility approximately twenty-two times that of aluminum hydroxide, while the former indicates a three hundred thousand fold difference in the solubilities of the two compounds. It will also be noted that there are minor differences in the order of the metals when arranged according to relative solubilities in the two lists.

TABLE 30

COMPARISON OF THE DETERMINATIONS BY BRITTON AND BY REMY AND KUHLMANN OF THE SOLUBILITIES OF HYDROXIDES

Hydroxide	Britton	Remy and Kuhlmann
$Mg(OH)_2$	6.9×10^{-4}	3.9×10^{-4}
$Al(OH)_3$	4.2×10^{-9}	1.8×10^{-5}
$Zn(OH)_2$	2.0×10^{-7}	3.6×10^{-5}
$Cd(OH)_2$	1.8×10^{-6}	3.7×10^{-5}
$Pb(OH)_2$	5.9×10^{-7}	5.6×10^{-5}
$Cu(OH)_2$	2.8×10^{-7}	6.9×10^{-5}

Remy and Kuhlmann were working under conditions such that carbon dioxide in the distilled water and in the air would exert a significant influence on the solubility of the hydroxides. On the other hand Britton was using a type of procedure in which such an effect would be negligible. Therefore, if the two sets of data represent correctly the actual solubilities under the divergent conditions, it is to be expected that the results of Remy and Kuhlmann should be higher than those of Britton. The fact that the figures for magnesium hydroxide do not bear out this prediction would suggest that there is something peculiar about magnesium hydroxide, or that the figures do not represent true solubilities under the conditions given. An actual solution of this matter really calls for experimental study, since it is possible to suggest ways in which either set of figures may be in error in the direction necessary to account for the irregularity observed. Thus Remy and Kuhlmann may not have allowed sufficient time for complete saturation of the solution. It will be recalled that their test for completeness of saturation was the fact that the conductance of the solution had reached a maximum. However, their experimental data showed that the conductance did not then remain constant but slowly decreased, due — as they explained — to absorption of carbon dioxide

which reacted with the hydroxyl ion forming bicarbonate or carbonate ion, thus replacing an ion of high mobility with one of much lower mobility. But it may be that the maximum obtained represented merely a condition in which the dissolving was being offset by the absorption of carbon dioxide, and that the solution was still distinctly unsaturated with respect to magnesium hydroxide. On this basis the solubility reported may be too low for the conditions of experimentation, thus accounting for a figure lower than that reported by Britton. On the other hand, if magnesium sulfate dissociates incompletely, or if magnesium ion combines with hydroxyl ion to form an intermediate ion, e.g., $MgOH^+$, the concentration of magnesium ion in the solution may be distinctly less than was assumed in the calculation of the solubility product of magnesium hydroxide. On this basis the value reported by Britton may be too high, thus accounting for a figure higher than the one by Remy and Kuhlmann.

In raising the question, which set of values is the more reliable, it will be obvious that the situation is much the same as in the case of the sulfides. It depends on the use to which the values are to be put. If one wishes to know how much of the hydroxide would dissolve in a liter of ordinary distilled water, without special protection from the air, undoubtedly the figure of Remy and Kuhlmann would be the more accurate, although even here the figure might be somewhat low. But if one wishes to know what separations might be carried out by precipitation with controlled concentrations of hydroxyl ion, the possibilities are indicated much more clearly by the figures of Britton than by those of Remy and Kuhlmann. The uncertainties in the carbon dioxide effect in the methods of Remy and Kuhlmann, make it impossible to distinguish between, or even to recognize, solubilities appreciably less than 1×10^{-6} molar. Britton's method, on the contrary, registers the same change in voltage of the cell when the solution changes from $pH = 3$ to $pH = 4$ as it does from $pH = 8$ to $pH = 9$. The chief chemical limitation on the experimental data (assuming that the electrodes themselves are functioning properly) lies in the difficulty of selecting the point on the curve at which precipitation starts. It must be observed, however, that the assumption that the effective concentration of the metallic ion is the same as the total concentration of the salt in the solution may be erroneous, and that such an error would cause the calculated solubility products to be too great. Certainly in the case of mercuric chloride, with excess chloride ion present, it is well known that the concentration of mercuric ion will be much less than the total concentration of mercury in the solution, therefore the correct figure for the solubility product of mercuric hydroxide must be considerably lower than the value given in the table. There is appreciable uncertainty as to the manner and extent of dissociation of salts containing ions of valence greater than one. Therefore, while the assumption of complete and direct ionization may be used in the absence of more accurate data, there is a distinct

probability that such an assumption introduces errors of varying magnitude for the different salts, some negligible and some significant. On that basis the differences observed by Britton may not be as accurate in individual cases as one might at first suppose.

§**41.** There have been considered several important papers dealing with the determination of solubilities of slightly soluble substances. It is hoped that the discussion has been presented with sufficient avoidance of technical detail so that the student has not been entirely lost in that side of the matter, but may have obtained a fairly clear notion, first, of the nature of the experimental data actually collected and second, of the method used to calculate solubilities from these data. Certainly it should be obvious that solubilities of slightly soluble substances are known with much less certainty than one might suppose from casually glancing at a solubility table.

In completing this discussion two questions might well be raised. First, how definitely are the solubilities of slightly soluble substances known? Second, to what extent is a solubility table useful in analytical chemistry?

In answer to the first question it may be said at once that the solubilities of salts derived from strong acids and strong bases are known with a fairly high degree of certainty through the range down to a solubility of approximately 1×10^{-6} M. Below that range the figures tend to indicate orders of magnitude rather than accurately known data. Further, the values for the salts in which both ions are univalent are more accurate than those in which either of the ions has a higher valence, particularly if the solubility is determined by an indirect method. The justification of this last statement is found in the second paper of Kohlrausch. It will be recalled that the following formula was proposed for calculating the equivalent conductance, Λ_N, at a particular concentration, N, from the mobility, Λ_∞, of the salt: $\Lambda_N = \Lambda_\infty - C\sqrt{N}$, in which C is an empirical constant. It was found that with univalent ions values could be set up such that for a particular salt the corresponding values for the ions could be added together to give the value of C for the salt in question. For bivalent ions, however, the values varied in different salts according to the particular combinations of ions present, so that each salt had to be considered individually.

In the case of salts derived from weak acids or weak bases (and to a still greater extent where both are weak), the situation is complicated by reaction of the salt with the solvent. Thus the metallic ion will combine to some extent with hydroxyl ion from the water to form a basic ion or metallic hydroxide, while the negative ion will combine to some extent with hydrogen ion to form an acid-ion or an acid. Either of these reactions will affect the solubility of the salt. If the solvent were always absolutely uni-

form in composition and if the extent of these reactions could be measured with sufficient accuracy, corrections could be applied that would not affect appreciably the accuracy of the solubility figure.

Within certain ranges, however, even distilled water is far from uniform in composition. Thus Kohlrausch in his earlier work used distilled water having a specific conductance which ranged between 2×10^{-6} and 3×10^{-6} and in his later work used still more carefully prepared water whose specific conductance ranged between 1×10^{-6} and 1.5×10^{-6}. In the course of one of the solubility experiments data were obtained which indicated a change in specific conductance of the water from 1.51×10^{-6} to 2.00×10^{-6}. Again, in Weigel's work on the sulfides, as shown in Table 22, the conductance of the water used ranged from 1.05×10^{-6} to 1.48×10^{-6}, and no evidence was submitted to show that this remained constant during the course of the experiment. From the fact that the product of concentrations of hydrogen and hydroxyl ions at 18° is approximately 1×10^{-14}, it is commonly assumed that for pure water the concentration of hydrogen ion equals the concentration of hydroxyl ion, both having the value 1×10^{-7} *N*. But carbon dioxide from the air dissolves in water to an extent varying with the partial pressure of the gas, and to a sufficient extent in any case to affect very considerably the concentrations of hydrogen and hydroxyl ions. Calculating the composition of the water as a dilute carbonic acid solution, the two limiting values for specific conductance of the water used by Weigel indicate differences in composition as follows:

Specific conductance	Concentration of H^+ moles per liter	Total concn. of carbonic acid, moles per liter
1.05×10^{-6}	2.94×10^{-6}	3.06×10^{-5}
1.48×10^{-6}	4.15×10^{-6}	5.93×10^{-5}

In the first case the concentration of hydrogen ion is 29 times and in the second case 41 times that assumed for pure water. Further, the second solution contains 2.9×10^{-5} moles more of carbonic acid per liter to react with the salt than does the first. It is obvious that, if significant reaction takes place, uncertainty will be introduced into solubility figures in the range from approximately 1×10^{-4} moles per liter on down, and that distinctions between solubilities below that range will be doubtful.

The fact that the normal impurity in distilled water is carbonic acid means that the solubility of salts derived from weak acids will be affected to a greater extent than those derived from weak bases. Further, the lower the concentration of carbonic acid in the distilled water the less will salts of the first type hydrolyze but the more will salts of the second type hydrolyze since lowering the concentration of hydrogen ion causes the concentration of hydroxyl ion to rise. The extent to which the salt of a

weak acid may undergo hydrolysis may be seen in the data of Weigel for manganous sulfide as recalculated for Table 26.

$$[Mn^{++}] = 1.17 \times 10^{-4}$$
$$[OH^-] = 7.35 \times 10^{-5}$$
$$[Mn^{++}] \times [OH^-]^2 = 6.35 \times 10^{-13}$$

On comparing this last number with the figure obtained from Britton's work for the solubility product of manganous hydroxide ($L_{Mn(OH)_2} = 5.1 \times 10^{-13}$) the two are found to be practically identical, thus showing that the manganous sulfide hydrolyzes and dissolves at least sufficiently to form a saturated solution of manganous hydroxide.

As another case of interest in this connection, attention may be directed to the question of the solubility of calcium carbonate in water. Johnston[1] pointed out that there can be no real equilibrium in aqueous solutions of carbonate except in the presence of a definite partial pressure of carbon dioxide in the atmosphere in contact with the solution and that any carbonate solution through which a stream of gas absolutely free from carbon dioxide is passed would gradually lose its carbonate and would ultimately contain only hydroxide. Therefore the solubility of calcium carbonate in pure water exposed to air free from carbon dioxide would be that corresponding to a saturated solution of calcium hydroxide, or approximately 2.3×10^{-2} moles per liter. If the solubility were being determined with distilled water, free from carbonate at the start, and the saturation were carried out in a completely filled and closed flask so that there would be no escape of carbon dioxide from the solution, the solubility would be approximately 1.6×10^{-4} moles per liter. On exposure to pure air of the usual composition (3 parts by volume of carbon dioxide in 10,000) the calcium carbonate would dissolve to the extent of approximately 6.0×10^{-4} moles per liter, this last increase being due, not to escape of carbon dioxide from the solution, but to the conversion of carbonate ion to bicarbonate ion through reaction of the salt with carbonic acid. From the solubility product of calcium carbonate ($L_{CaCO_3} = 9.8 \times 10^{-9}$, is the figure used by Johnston) the solubility of calcium carbonate would be approximately 1×10^{-4} moles per liter if there were no reaction with the solvent.

If the above discussion has over-emphasized the part which carbonic acid plays in the solvent action of distilled water of purity higher than that usually available for the analytical chemist, the impression may have been gained that if the carbonic acid were eliminated one would have an inert solvent in which true solubility values could be obtained.[2] It is

[1] Johnston, *J. Am. Ch. Soc.*, **37**, 2020 (1915).

[2] An interesting paper by Kolthoff, *J. Phys. Ch.*, **35**, 2711–21 (1931), starts with selected values for the solubility products of the sulfides and calculates the corresponding

possible to prepare distilled water free from carbon dioxide and to preserve it in this condition, though this is not a simple process if the water is to be transferred from one piece of apparatus to another. But calculations will show that for salts of very weak acids and for hydroxides of low solubility even pure water containing no carbonic acid would not be an inert solvent. Thus in the case of salts derived from weak enough acids so that significant reaction would occur with a concentration of hydrogen ion of 1×10^{-7} *M*, the actual solubility measured would be the true solubility plus the chemical solubility due to reaction with the solvent. Under such conditions the total value may be extremely large as compared to that which would be obtained if the solvent were really inert. This is the situation that actually exists for many of the sulfides and carbonates, and would undoubtedly be shown with still other salts if sufficiently accurate experimental data were available. In the case of hydroxides the presence of hydrogen and hydroxyl ions to the extent of 1×10^{-7} moles per liter means that significant effects may be expected if the solubility of the hydroxide is less than 1×10^{-6} moles per liter. Thus toward hydroxides having solubilities in the neighborhood of 1×10^{-7} moles per liter, the water is a strong enough acid to produce appreciable increase in solubility due to neutralization. On the other hand, with hydroxides having solubilities distinctly below 1×10^{-7} moles per liter the water is a strong enough base so that appreciable repression of solubility by the common ion effect would be expected. Thus for a true solubility of 1×10^{-8} moles per liter for a hydroxide of the type $M(OH)_2$, the presence of 1×10^{-7} *M* hydroxyl ion should lead to an actual value only 0.01 that of the true solubility. It is obvious therefore that direct experimental measurements of the actual solubility of the extremely insoluble hydroxides in water would not give the true solubility directly, but would give values which would need to be subjected to various mathematical operations before a number could be obtained to be inserted into a table of true solubilities. It is also apparent that much of the confusion existing in the discussion of the accuracy of the solubility data in the literature is due to failure to distinguish the actual solubility in a particular solvent from the theoretical (or hypothetical) solubility that the compound would have if the solvent were really inert (in the case of water, serving only as an ionizing medium for the electrolyte in question).

Thus the two utterly discordant sets of data for the sulfides represent chiefly the differences between actual solubility and ideal solubility. A re-examination of the results of re-calculating Weigel's data will make this clear. If the usual value is assumed for the secondary ionization of hydrogen sulfide,

$$K_{HS^-} = 1.2 \times 10^{-15}$$

solubilities in CO_2-free distilled water and in "equilibrium water" (distilled water containing sufficient CO_2 to be in equilibrium with normally pure air), assuming that reaction takes place between sulfide ion and hydrogen ion in the solution.

and the values for the concentrations of hydrogen and bisulfide ions in the saturated lead sulfide solution ($[H^+] = 4.51 \times 10^{-5}$, $[HS^-] = 1.23 \times 10^{-6}$) are inserted in the usual formula the following value is obtained:

$$[S^{--}] = 3 \times 10^{-15}$$

The concentration of lead ion in the solution was calculated to be

$$[Pb^{++}] = 7.4 \times 10^{-6}$$

According to the usual practice the concentration of sulfide ion would be taken as the true solubility of lead sulfide in this particular solution, so the difference between that and the concentration of lead ion represents the chemical solubility of the lead sulfide due to reaction of the salt with the solvent, with production of bisulfide and bicarbonate. The actual solubility of lead sulfide in distilled water of the composition given is undoubtedly fairly close to 7.4×10^{-6} moles per liter, but the true solubility in water as an inert solvent is probably somewhere near the square root of the product of concentrations of lead and sulfide ions, or approximately 1.5×10^{-10} moles per liter.

It will be noted, then, that experiments involving the study of saturated solutions, in distilled water, of salts of weak acids or bases (especially acids) are incapable of recognizing or distinguishing between orders of solubility much less than 1×10^{-4} moles per liter. Yet the results of Britton on the hydroxides and of Bruner and Zawadzki on the sulfides suggest solubilities many thousand fold less than this. It is an obvious question to ask, how could such values be determined, and how reliable are they? An examination of the papers in which the experimental methods are given shows that these low values were calculated by the use of the solubility product principle. This principle, it will be recalled, assumes that there is a definite product of concentrations of the ions of a salt which characterizes any saturated solution of the compound. Therefore if saturated solutions of the compound can be prepared in which one of the ions is present in sufficiently high concentration so that it may be estimated directly, and if the concentration of the other ion may be calculated from other experimental data about the solution with the aid of known ionization constants, numerical values will be obtained which may be multiplied together in the usual way to give what is known as the solubility product of the compound. From this the molar solubility is calculated by the application of the proper one of the following formulas:

$$S_{AB} = \sqrt{L_{AB}}, \quad S_{A_2B} = \sqrt[3]{\frac{L_{A_2B}}{4}}, \quad S_{A_2B_3} = \sqrt[5]{\frac{L_{A_2B_3}}{108}}, \text{ etc.}$$

In this calculation the assumptions are made that there is always a normal repression of solubility by the common ion effect and that there is no

irregularity introduced by the presence of relatively high concentrations of other substances in the solution. One does not need to look far into direct experimental data bearing on these two assumptions to realize that neither of them expresses the truth with any high degree of accuracy.

Take the case of silver chloride, one of the classic examples used to illustrate the solubility product principle. The solubility of this salt in water is approximately 1×10^{-5} moles per liter. From this one would calculate, by the application of the solubility product principle, that the solubility in 0.01 *M* hydrochloric acid should be only 1×10^{-8} moles per liter. Experimentally, however, the minimum solubility in the presence of excess of chloride ion appears to be approximately 2×10^{-7} moles per liter.[1] Or, consider the data for calcium sulfate. Having a solubility of 1.5×10^{-2} moles per liter, its solubility product would be 2.25×10^{-4}, and the solubility in half molar sodium sulfate should be reduced to approximately 4.6×10^{-4} moles per liter. Actually, however, the minimum solubility at the most favorable concentration of sodium sulfate is 1.0×10^{-2} moles per liter. Finally, as a more extreme case, consider lead chloride. Having a molar solubility of 3.5×10^{-2}, approximately half the amount in solution should precipitate on the addition of 2 cc. of molar lead nitrate solution to 10 cc. of a saturated lead chloride solution. But, as a matter of experiment, not only will no precipitate form, but the solution will actually be slightly less than saturated with respect to lead chloride. If cases of this sort are other than rare exceptions one must recognize the possibility of error in results calculated in that way unless there are reasonable accompanying data to show that the calculation is justified in each particular case. In the absence of such confirmatory evidence the solubility product principle may be in the nature of a crutch enabling an invalid to hobble about who must otherwise stay confined to his room.

As to the second of the two assumptions used in the calculations in question; namely, that there is no irregularity introduced by the presence of relatively high concentrations of other substances in the solution, attention has already been called to the fact that the concentration of mercuric ion in a solution will be affected to a very considerable extent by the presence of chloride ion. This, however, is a fairly obvious case. But one may examine the available data concerning the effect of accessory ions on any of the common precipitates and find that these all show solvent action varying from case to case. Thus, the solubility of barium sulfate in hydrochloric acid (which is appreciable even in 0.1 *N* hydrochloric acid and still more pronounced in the normal acid) is commonly ascribed to the reaction of hydrogen ion with the sulfate ion to form acid-sulfate ion.

[1] Forbes and Cole, *J. Am. Ch. Soc.*, **43**, 2496 (1921), reported a calculated minimum value of 0.025 mg. per liter; Richards and Wells, *J. Am. Ch. Soc.*, **37**, 487 (1905), measured the solubility experimentally and found 0.03 mg. per liter.

Nitric acid is approximately the same strength as hydrochloric acid, yet it exerts distinctly greater solvent action on barium sulfate than does hydrochloric acid. The figures are given in Table 31.

TABLE 31

SOLUBILITY OF $BaSO_4$ IN DILUTE ACIDS AT 20°

Solvent	Solubility, mg./l.
H_2O	2.3
1 *N* HCl	89.0
1 *N* HNO_3	107.0

It is evident that the nitrate and chloride ions have something to do with the solubility of barium sulfate. Or, examine the curves in the paper by Kendall and Sloan[1] showing the effect of various metals on the solubility of silver and lead chlorides in chloride solutions. Even metals as similar as sodium and potassium, or barium and calcium show readily measurable differences. Therefore it is difficult to believe that the chloride, nitrate, sulfate or other ions present exert either negligible or equal effects on the solubilities of the various hydroxides or sulfides studied.

The question of experimental accuracy has not been raised in this discussion, but it may be interesting to note that in the work of the type of Bruner and Zawadzki and of Britton, experimental error usually affects the logarithm of the result rather than expressing itself directly in the result. Thus, for Britton's determination of the E.M.F. of the cell when magnesium hydroxide starts to precipitate, if, instead of the value 0.892 volt, 0.834 volt were obtained, this would not mean a simple error of 6.5% in the final calculation. On the contrary, it would lower the *p*H one whole unit, would make the concentration of hydroxyl ion ten times as great, and would increase the solubility product a hundred fold.

From the above discussion it will be evident that while there are indications of orders of solubility among the common precipitates far lower than can be measured by the more direct methods, there is actually considerable doubt as to the accuracy with which the indirect methods give the correct values in individual cases. It is true that the wide spread of the values thus obtained affords a fairly simple explanation of some of the separations obtained by controlling the concentration of the precipitating ion. But this simplicity is no guarantee that this explanation is correct or that it tells the whole story. As a matter of fact there is a considerable amount of evidence available which indicates that analytical separations may involve much more than just differences of solubility.

[1] Kendall and Sloan, *J. Am. Ch. Soc.*, **47**, 2308, 2310, 2314 (1925).

§42. Let us now turn to a brief consideration of the second question — to what extent is a solubility table useful in analytical chemistry? The immediate answer is that a solubility table shows the more obvious possibilities of separations by precipitation, and indicates others where fair separations may be possible if the conditions can be adequately controlled. The ideal situation in chemistry is one which permits an accurate separation in a single operation, without special precaution as to the concentration of the reagent used or the amount to be added in excess. Such a result would be expected if one of the compounds were slightly enough soluble so that the amount remaining in solution might be considered negligible, while the other were sufficiently soluble so that none would precipitate when a moderate excess of the reagent is added.

In order to discuss the completeness of precipitation that may be expected, it is convenient to divide the whole range of solubility into several arbitrary classes. The two terms, soluble and insoluble, may be used to name the classes at the two ends, with qualifying words added to distinguish between the intermediate classes. In Table 32, five classes are defined.

TABLE 32

CLASSES OF SOLUBILITY

Decreasing order of solubility	Name of class	Range of solubility
1	Soluble	more than 50 g. per liter
2	Moderately soluble	10–50 g. per liter
3	Slightly soluble	1–10 g. per liter
4	Moderately insoluble	0.01–1 g. per liter
5	Insoluble	less than 0.01 g. per liter

One may give these classes an analytical significance as follows:[1]

(a) Salts in class 1 are sufficiently soluble so that no precipitate will form even when the reagent is added in moderate excess to a fairly concentrated solution.

(b) Salts in class 2 are sufficiently soluble so that ordinarily no precipitate will form, but that a precipitate *may* be obtained if the reagent, in fairly high concentration, is added in excess to a fairly concentrated solution.

(c) Salts in class 3 are of an intermediate solubility such that a precipitate will form if the reagent, in moderate concentration, is added in excess to a solution containing the metallic ion in moderate concentration. However, such precipitation, even at best, will usually leave significant

[1] The solution to which the reagent is added contains a soluble, highly ionized salt of the metal, and the reagent added is a soluble, highly ionized salt of the acid radical.

amounts of the metal in solution. Further, no precipitate will form if either the reagent or the metallic salt is used in low concentration.

(d) Salts in class 4 are slightly enough soluble so that they will precipitate readily even from fairly dilute solution when the reagent is used in moderate concentration. Under favorable conditions precipitation may be sufficiently complete so that the amount remaining in solution will be negligible. However, if the reagent lends itself to such treatment, it may be possible to prevent precipitation by setting up in the solution, before the reagent is added, special unfavorable conditions; such as having the solution appreciably acid while using the anion of a weak acid as the precipitating agent.

(e) Salts in class 5 are slightly enough soluble so that precipitation will take place readily and completely under ordinary conditions, providing the reagent is added in slightly more than equivalent amount. Only under extraordinary conditions, such as extreme dilution of the solutions or unusual repression of ionization, etc., will precipitation be incomplete or fail to occur.

From such a classification it will be obvious that one should expect to obtain a satisfactory separation in one operation if the less soluble salt were a typical member of class 5 and the more soluble salt were a typical member of class 1 or 2. Further, with moderate attention to details it would appear possible to separate typical salts of class 4 from those of class 2, and salts of class 5 from those of class 3. In these cases it will be observed that there is a solubility difference ranging from a thousand fold or more down to approximately a hundred fold. On the basis of solubility, therefore, it would appear that the possibilities of analytical separations were pretty well defined.

It is well known, however, that the solubilities of slightly soluble compounds are generally decreased by the addition of excess of the precipitating agent. This effect may be sufficiently marked to change the classification of a salt, shifting a moderately insoluble compound to the insoluble class, or shifting a slightly soluble compound to the moderately insoluble class. It would be very useful if there were available an adequate means for calculating the magnitude of this effect, so that one might add a definite excess of the reagent and then be able to use the data of the solubility table to figure the completeness of precipitation in the resulting solution. The usual attempt to make calculations of this sort is based on the solubility product principle. This principle assumes that, while the solubility varies with excess of common ion, the product of concentrations of the ions of a salt (in the mathematical formula the individual concentrations are raised to powers equal to the numbers of the corresponding ions derived from one molecule of the salt) will be the same in all saturated solutions of the salt, providing the solutions are at the same temperature. On this basis, if one were to add to a saturated aqueous solution of a

salt of the type AB($AB \rightleftarrows A^+ + B^-$) sufficient reagent supplying B^- to establish a concentration of B^- double that in the simple solution, the concentration of A^+ should be reduced to half what it was. Since the solution was saturated at the start, this would mean that half the A^+ would precipitate as AB, and if AB is regarded as essentially completely ionized this should lower the solubility of the compound to half of what it was.

If precipitations occurred in accordance with these predictions based on the solubility product principle, considerably smaller differences in solubility than are indicated above might still prove effective for purposes of analytical separations. Suppose, for instance, the difference in solubility of two salts, AB and A′B, were only tenfold. When sufficient of the reagent is added so that the concentration of anion is equal to that of a saturated solution of the more soluble salt, the concentration of the anion will be ten times as great as that characteristic of a saturated aqueous solution of the less soluble salt. This should result in a tenfold decrease in the solubility of the latter, so the theoretical ratio of solubilities of the two compounds under such condition should be 100 : 1 instead of 10 : 1. For compounds of the type AB_2 (or AB_3), a tenfold difference in solubility in water of two salts would mean that the introduction of sufficient B^- to be equivalent to the concentration of the cation of the more soluble salt in a saturated aqueous solution should produce a thousand fold (or ten-thousand fold) difference in concentrations of the cations of the two salts. On this basis, it might be feasible to separate metals from each other by conversion to salts of identical solubility in water (or even when the solubility of the salt to be left in solution is somewhat less than that of the one to be precipitated) if the salts are of different types (A_2B, AB, AB_2, AB_3, etc.), through differences in the reduction of solubility by a given excess of the precipitating agent.

One frequently runs across cases where reduction in solubility by relatively high concentration of one of the ions results in precipitation of salts which may not have been expected. Thus, in the test for a sulfate by adding barium nitrate to a nitric acid solution of the unknown, it is entirely possible to be sufficiently careless in the amount of nitric acid present, and in the concentration and volume of the barium nitrate added, to obtain a finely divided white precipitate of barium nitrate in spite of the fact that barium nitrate is sufficiently soluble in water to belong in class 1. Again, in the removal of iodide and bromide by oxidation in the presence of sulfuric acid before testing for chloride with silver nitrate, sufficient sulfate may be present so that the thoughtless use of silver nitrate may result in the formation of a white granular precipitate of silver sulfate. In the precipitation of Group I with hydrochloric acid a similar situation is involved in the case of lead, although familiarity with the fact that lead may be found in Group I may cause one to forget that

there is anything remarkable about this. Actually, however, the solubility of lead chloride places it in the moderately soluble class, somewhat near to the line between moderately and slightly soluble. In the precipitation of Group I, the reagent used is commonly of sufficient concentration to accomplish a considerable repression of solubility of lead chloride, so that in this solution it may belong in the slightly soluble class, not far from the line between slightly soluble and moderately insoluble. Thus it is not surprising that the addition of 5 *N* hydrochloric acid to a 0.25 *N* lead nitrate solution produces a copious precipitate of lead chloride. But if one used a solution of hydrochloric acid more nearly equivalent to that of other common precipitation reagents (0.25 − 0.5 *N*) no precipitate of lead chloride would form so long as the concentration of chloride ion in the solution was kept below 0.1 *N*.

It was suggested above that it would be extremely useful if methods of calculation were available so that the solubility in the presence of various reagents could be derived from the data of a solubility table. But attention has already been called to the fact that the solubility product principle offers only moderate assistance in this matter.

Over any considerable range of compounds it will be found that the solubility product principle has little quantitative validity and occasionally may even fail qualitatively to predict the experimental change in solubility. Further, as a matter of fact, cases are not difficult to find, in which separations are not only possible in spite of unfavorable solubility relations, but also impossible in spite of favorable solubility relations. Cases of the first sort usually involve the fact that individual compounds show marked differences in the rate of precipitation, a factor which is not related directly to the corresponding solubilities. In favorable cases, precipitation may take place so slowly that only a negligible amount will be formed in the time allowed for the precipitation and removal of the other compound. In the separation of Group II metals from zinc by precipitating with hydrogen sulfide in 0.25 *N* hydrochloric acid solution, the slowness of precipitation of zinc sulfide is a significant factor in the results obtained. Again, in the quantitative determination of calcium in a solution containing moderate amounts of magnesium, the fact that a saturated solution of magnesium oxalate contains only about 65 mg. of magnesium per liter, would seem to make it impossible to carry out a successful separation in a single operation by precipitation with ammonium oxalate. Yet this is the standard method of separating calcium from moderate amounts of magnesium, and it depends for its effectiveness on the extreme slowness with which the magnesium oxalate precipitates.

As instances of the second sort, in which separations fail in spite of favorable solubility relations, two cases may be mentioned. The molar solubility of strontium sulfate is about 0.04 that of calcium sulfate. On that basis, if the solubility product principle worked, one might expect to

get a separation permitting strontium to precipitate without contamination by calcium down to a mole ratio of 1 part of strontium to 625 parts of calcium. But direct experiments show that with dilute ammonium sulfate (0.1 *N*) strontium sulfate precipitates readily on heating only down to a concentration corresponding to that of a saturated solution of strontium sulfate in water. With calcium sulfate, likewise, there is relatively slight repression of solubility by excess of ion; actually supersaturation manifests itself to such an extent that it is possible to add to a 0.2 *N* solution of calcium chloride an amount of reagent sufficient to produce a concentration of sulfate ion equal to that of a saturated aqueous solution of calcium sulfate (0.03 *N*) without precipitation occurring within an hour's standing or by any ordinary treatment of the solution. In terms of solubility product, this corresponds to a product of concentrations of ions about seven times that characteristic of a saturated solution of calcium sulfate. The interesting situation is thus presented that while relative solubilities would lead one to expect a separation in one operation down to a mole ratio of 1 part of strontium to 25 of calcium; and relative solubility products would lead one to expect a separation to 1 part in 625 ($1 : 25^2$); the supersaturation effects would lead to a ratio of approximately 1 : 175. With such divergences indicated by individual experiment and by theory, the obvious suggestion is to try the separation directly and see how it works. One mg. of strontium in 10 cc. forms a readily visible precipitate on adding 5 cc. of 0.1 *N* ammonium sulfate solution and heating to boiling. But the addition of 40 mg. of calcium to the solution prevents the precipitation of the strontium sulfate. As a matter of fact, no precipitate will form with 5 mg. of strontium in the presence of 40 mg. of calcium, and precipitation takes place slowly even with 10 mg. of strontium present. Five mg. of strontium to 40 mg. of calcium represents a mole ratio of approximately 1 : 20, a ratio less favorable even than the solubility difference indicated above. It is evident that calcium ion interferes with the precipitation of strontium sulfate to an extent that more than fully offsets the advantage which the supersaturation effect would appear to give.

The second illustration has to do with these same two metals, strontium and calcium, but is concerned with the problem of precipitating strontium sulfate completely enough to avoid any interference of strontium with the test for calcium, and at the same time to leave sufficient calcium in solution so that it may be identified readily. It is possible in this procedure to use excess of sulfate ion so the difficulty noted above in the precipitation of strontium sulfate in the presence of calcium will no longer be encountered. Further, it might appear that there is no choice among the common reagents as to whether one uses sodium, potassium, or ammonium sulfate for the purpose. All three are readily soluble, and all are highly ionized salts, therefore any one of the three would seem to be satisfactory

for the purpose. But when experimental studies are examined showing the effect of excess of sulfate on the solubility of calcium sulfate, it is found that potassium sulfate behaves differently from the other two. With ammonium sulfate, for example, as increasing amounts are added, the solubility of calcium sulfate reaches a minimum about two-thirds that in pure water, then rises again until the solubility becomes considerably greater than in water. But with potassium sulfate, while the solubility curve starts out very much like the other, reaching a first minimum and starting to rise again, the curve changes abruptly shortly beyond this point, the solubility of the calcium sulfate decreasing steadily with further addition of potassium sulfate due to the formation of the slightly soluble double salt, syngenite ($K_2Ca(SO_4)_2 \cdot H_2O$). Thus, with excess of a moderately concentrated potassium sulfate reagent the calcium may be removed very largely from the solution.

From this discussion it should be realized that, while in many cases there is a direct relation between separations that work and solubilities of the compounds involved, there is no guarantee in individual cases that separations will work where there are wide differences of solubility, or that separations will fail where there are slight differences of solubility. This is a fact not infrequently forgotten even by the analytical chemist, who sometimes recommends methods on the basis of experimental tests on the individual metals, without checking the method for its accuracy over a fair range of mixtures of the metals in question.

If in the last few pages it seems as though the importance of a solubility table has been underrated, the defence may be made that this has been done intentionally to counteract the point of view that a solubility table is a complete and adequate basis for analytical separations by precipitation; a point of view reflected in the common statement that qualitative analysis is merely a matter of relative solubilities. Actually, of course, the solubility table represents an important set of data for the analytical chemist. It is distinctly incomplete, however, and reservations must be made as to the accuracy of the figures in the lower ranges. Further, the fragmentary data available dealing with the solubility of salts in the presence of other salts indicate that there are several factors at work which may sometimes reinforce and sometimes counterbalance each other, and which may also be difficult to evaluate quantitatively.

The common experience that the solubility of a compound is usually decreased by the addition of a reagent supplying an ion in common with the first compound developed into the solubility product principle. This principle assumed that the effect of other materials in the solution could be disregarded, and that the salt would behave as a normal, reversible system in which the concentration of one of the components had been changed by the addition of the common ion. Assuming the validity of the law of mass action; if the solution was saturated before the second salt

was added, it should be a simple matter to calculate the extent to which equilibrium was disturbed by the given change in concentration of the one ion and, from this, the extent to which the salt should precipitate in order to restore chemical equilibrium. The fact that these calculations at best yielded only approximations was early recognized. It was then suggested that the quantities to be used in the calculations were not the concentrations of the ions but their "active masses," and the attempt was made to set up "activity coefficients" for the various ions by which active mass could be calculated from concentration and vice versa. These have not proved entirely successful. Later it was observed that the chemical behavior of ions in solution seemed to be affected to some extent by the presence of other ions. Considerable success was achieved by relating this to the electrical environment set up in the solution by the presence of the various ions both of like and of unlike sign. Out of this developed the interionic attraction theory which suggested that one should expect the solubility product of a compound to increase with increasing ionic strength of a solution. This theory is not completely developed as yet, and must obviously take into account more than just the electrical charges on the ions if it is to become generally useful. For instance, the basic strength of the metal accompanying the common ion has something to do with the stability and solubility of the corresponding double salt. Further, there is no obvious basis for predicting the formulas of complex ions in solution or for calculating the extent to which the formation of these will affect the solubilities in question. And, finally, the facts of slow precipitation and of co-precipitation — the carrying down by precipitates of materials which are supposed to be soluble under the given conditions — are not on a satisfactory basis, either practically or theoretically. It is evident, then, that the experimental solubility data are incomplete and the various factors affecting solubility in complex solutions are not known with sufficient accuracy to permit adequate calculations from the existing data. Under such circumstances it is clear that the ultimate test of a proposed separation is not that it satisfies the data of the solubility table, but that it works.

It has seemed best not to expand this section sufficiently to treat the above factors even in outline. Such material belongs in more advanced studies, along with a critical examination of the formulas used in the calculation of solubilities from experimental data, and a consideration of the validity of the measurements made.

THE DELICACY OF PRECIPITATION AND COLOR REACTIONS OF THE METALS

§**43.** The difference in readiness with which metals precipitate with given reagents is the basis of most of the separations in analytical chemistry. After the separations have been carried out, the formation of a further precipitate or colored compound by addition of another reagent is the common method of proving the presence of each of the metals. In order to use a scheme of analysis intelligently it is necessary to know the limits within which the given procedures will work. There are many statements in the literature giving the sensitivity of various tests, but much of this is not immediately applicable in the ordinary scheme of qualitative testing either because the conditions under which these values were obtained are not given or because some of the conditions are so exacting or time consuming as to be unsuited for routine use in an introductory course.

The following material presents the sensitivity of the common reactions obtained by experimental study under reasonable student working conditions. Standard solutions of the metallic salts were prepared of such concentrations that 1 cc. contained 20 mg. of the metal. Two cc. of each solution was then placed in a graduated cylinder, diluted with water to 20 cc., poured into a six-inch test tube, then poured back and forth from test tube to graduate eight or ten times to produce uniform mixing, and finally divided equally between the test tube and the graduate. The test tube, containing 10 cc. of solution, was placed in a test tube rack in position number 1. The solution in the graduate was diluted with water to 20 cc. and the above process repeated. The second test tube with its 10 cc. of solution was placed in position number 2. This was continued until 10 or 12 dilutions were prepared, the first containing 20 mg. of the metal in 10 cc. and each one after that having half the concentration of the preceding one. The quantities thus present in the individual tubes are indicated below.

Tube No.	1	2	3	4	5	6	7	8	9	10	11	12
Mg. in 10 cc.	20	10	5	2.5	1.25	.63	.31	.16	.08	.04	.02	.01

The questions of what strength of reagents to use and how much to add were answered in rather arbitrary fashion. Theoretically, if the behavior of different metals with a given reagent are to be compared, the quantity of reagent added should be adjusted in each case to the amount of metal present, using either an equivalent amount of reagent (or some multiple of this) or such an excess as will bear a definite relation to the

solubility of any precipitate formed. Since the data on solubility of precipitates are in many cases only rough approximations it is impossible to make an adjustment of the last type. Further it is doubtful if the value of the results would warrant the immense amount of labor involved in making adjustments of the first sort for each metal and for each of the different dilutions. Therefore it was decided to use uniform quantities of commonly available reagents. Certain of these, e.g., dil. HCl, dil. NH_4OH, H_2O_2, etc. are found in the ordinary laboratory in higher concentrations than can be had for several of the salts. In such cases it was decided to employ the available reagent rather than prepare a special reagent for this series of tests. With the common salts, however, it was necessary to prepare stock solutions, and in these cases the concentration was put at 0.5 *M*, or as near that as the solubility of the salt would permit. With liquid reagents the volume added was normally 0.5 cc., while with H_2S, delivered at the rate of 60 cc. per minute, the time of treatment was normally 30 seconds for acid solutions and 15 seconds for alkaline solutions.

It is obvious, at once, that the conditions employed are probably not those necessary to give the maximum delicacy of test in any particular case. But the results do give a basis for comparison of reactions where only general directions are being followed, and the table may well serve as a starting point from which the effect of various factors such as temperature, volume of solution, concentration of reagent, use of accessory reagents, etc. might be studied.[1]

On examining the table in some detail certain facts are noted that are somewhat surprising. Even in the more sensitive reactions a general limit of visibility, whether of colored solution or of precipitate, seemed to be reached at approximately 0.01 mg. of metal. If one remembers that tube 6 = 0.6 mg., 8 = 0.16 mg., 10 = .04 mg., and 12 = .01 mg., and then glances through the table he will be struck by the infrequency of cases in which tubes numbered above 10 show visible effects. It is, of course, frequently possible to recognize a smaller quantity of material than this, but in such cases special technique is commonly necessary, such as concentration to small volume, examination with special lighting, use of microscope, etc.

Another fact to be noted is that there is no obvious relation between sensitivity and equivalent weight or atomic weight of the metals involved. Compare the reactions of such heavy metals as silver, barium, mercury, lead and bismuth, with those of magnesium, aluminum and calcium. One might expect that it would take approximately the same number of molecules (or, possibly, equivalents) combined into a molecular aggregate,

[1] As a matter of opinion, a moderate amount of just such study, resulting in an appreciation of the range of specific differences in the effects noted, might well be substituted for some of the routine work of the ordinary course in qualitative analysis.

to produce a visible particle, regardless of the molecular or equivalent weights of the materials. On this basis there should be a definite trend toward greater sensitivity of test in the case of the lighter metals. (That is, if sensitivity is defined as the least weight of the substance that will produce visible effect in a given volume. If sensitivity were calculated in terms of equivalent or molecular weights, one would expect a corresponding trend toward equal sensitivity for all metals.) In the experiments listed in the table, bismuth (atomic weight = 209) shows visible precipitation with NH_4OH at dilutions in which aluminum (atomic weight = 26.97) fails. Barium (atomic weight = 137.37) shows approximately the same (or slightly greater) sensitivity toward precipitation in the form of sulfate as calcium (atomic weight = 40.07) does toward precipitation as the oxalate. It appears as if the atomic weight may have something to do with the opacity of a precipitate, and hence with the visibility of very small amounts.

The argument may be advanced that in the last paragraph no account was taken of the relative solubility of the different precipitates, that bismuth hydroxide and barium sulfate may be less soluble than aluminum hydroxide and calcium oxalate, and that a limit will be reached with the solubility of the compound, in every case, at which no precipitate will form to be visible. In commenting on this argument it must be acknowledged, of course, that solubility does have something to do with the possibility of obtaining visible precipitation at a given dilution. For appreciably soluble precipitates this is a very important factor. But if the table is consulted again it will be found to contain a number of cases where the relative sensitivities of precipitation are contrary to the commonly accepted values for solubilities. Thus, cadmium and lead sulfides are considered to have approximately the same solubility, yet visible effects were obtained with hydrogen sulfide in the case of lead for several dilutions beyond the last in which cadmium showed precipitation. Not only in the case of cadmium, but even in the case of mercury was the delicacy of precipitation with hydrogen sulfide less than that of lead; and yet mercuric sulfide is considered to be much less soluble than lead sulfide. This same irregularity is noted again with zinc and manganese. Zinc sulfide is much less soluble than manganous sulfide, yet the latter showed definitely at dilutions beyond the last in which zinc sulfide appeared.

The explanation for such irregularities may be found in two factors which are sometimes lost sight of in discussions of the theory of qualitative analysis. One of these is the fact that in very dilute solutions many precipitates are slow to form. A condition of supersaturation may persist for a long time, and the extent of supersaturation necessary for prompt formation of a precipitate will vary considerably in individual cases. Thus, Smith[1] reports the work of von Weimarn in studying the precipitation of

[1] Smith, T. B., "Analytical Processes," Longmans, Green & Co., New York, **1929**, 41.

barium sulfate as follows: with an amount of barium sulfate twenty-six times as great as should stay in solution it took five minutes for the solution to show opalescence; whereas with only five times as much present as the solubility a precipitate appeared only after a month.

The other factor is related to the variation in visibility which the same substance may show according to its method of preparation and state of subdivision. A well known instance of this is found in the difference in ease of recognizing a few hundredths of a milligram of silver chloride in the form of an opalescent suspension and as a coagulated precipitate. A less familiar case is that of aluminum hydroxide as precipitated from acid solution on the one hand and from alkaline solution on the other. Precipitating from aluminum chloride solution with ammonium hydroxide, the usual, semi-transparent, gelatinous precipitate is obtained. On adding excess of ammonium chloride to a solution of sodium aluminate, containing a corresponding amount of aluminum, a much more opaque, flocculent precipitate is obtained.

This last experiment may be carried out in such a way as to eliminate any significant difference in the final solutions by using the same reagents, aluminum chloride, sodium hydroxide, and ammonium chloride in the same amounts, but varying the order of mixing to obtain the two precipitates. Thus, 2 mg. of aluminum (in the form of aluminum chloride solution) in 10 cc. volume may be treated with 2 cc. of 5 N NaOH solution and then 5 cc. of 5 N NH_4Cl solution added, or the aluminum chloride solution may be treated with a mixture of 2 cc. of 5 N NaOH and 5 cc. of 5 N NH_4Cl. The resulting precipitates may be examined by looking down into the test tubes or by letting the precipitates settle and then holding the tubes up to the light. In either case a marked difference in ease of distinguishing the precipitates will be noticed.

With differences of the above sort easily demonstrated for many of the common precipitates, it is not difficult to believe that the ordinary mixing of reagents may result in setting up conditions that favor visibility for one precipitate much more than for another. In considering the problem of sensitivity of tests there is clearly much to be done by way of determining the conditions for the formation of individual precipitates that will favor maximum visibility. Little attention has been paid to this question in the past, yet it is a factor only less important than solubility in determining the sensitivity of a precipitation reaction. It is necessary to form enough of the compound so that precipitation will take place, and in addition it is necessary to form enough of the precipitate so that it can be seen, if the precipitation reaction is to produce a visible effect. In the case of relatively insoluble compounds it may well be that a much larger quantity is required for visibility than is needed to exceed the solubility. Under such conditions it is entirely possible that a precipitate of moderate insolubility, but high visibility, may appear at dilutions below that at which a less

soluble and less visible precipitate can be seen. Possibly this is the explanation for some of the irregularities noted above. Perhaps under favorable conditions the various precipitates may be obtained with equal or equivalent visibility, but under ordinary conditions marked differences are observed.

In closing this brief discussion of the table of sensitivities, a further word of caution must be added. The table cannot be used directly as a basis for analytical separations. There are complexities about separations, such as side reactions, co-precipitation, and interference of materials with normal precipitation of various substances, that make it imperative to try out any proposed scheme with known mixtures before using it on unknown material. Sometimes the separations work "according to theory," frequently they do not, and much of the confusion in the literature of chemical analysis is due to failure to check the method with standard materials. This word of caution is not intended to discourage the student from figuring out possible alternative methods of separation from such experimental work as is given in the table; it is intended, rather, to emphasize the necessity of regarding such alternative procedures with candid scepticism until they have been tested experimentally.

TABLE 33

§44. Sensitivity of Common Precipitation Reactions and Color Effects (10 cc. volume)

Metal	Reaction	Special conditions	Effects observed in the tubes containing the lower concentrations of metal
Ag	$AgNO_3 + HCl$	add 0.5 cc. 5 *N* HCl	9 = slightly cloudy, 10 = barely visible opalescence.
	$Ag(NH_3)_2Cl + HNO_3$	add 0.5 cc. 5 *N* HCl + 3 cc. 5 *N* NH_4OH, then 5 cc. 5 *N* HNO_3	9 = slight opalescence, 10 = clear.
	$Ag(NH_3)_2Cl + KI$	add 0.5 cc. 5 *N* HCl + 3 cc. 5 *N* NH_4OH, then 0.5 cc. 0.5 *N* KI	13 = very slight opalescence, 14 = clear.
Hg (ous)	$Hg_2(NO_3)_2 + HCl$	add 0.5 cc. 5 *N* HCl	8 = slight opalescence, 9 = clear.
	$Hg_2(NO_3)_2 + NH_4OH$	add 0.5 cc. 5 *N* NH_4OH	6 = slight brownish cloudiness, 7 = barely visible color.
	$Hg_2Cl_2 + NH_4OH$	add 0.5 cc. 5 *N* NH_4OH to ppt. on filter	7 = visible black stain, 8 = no discoloration.
Pb	$Pb(NO_3)_2 + HCl$	add 0.5 cc. 5 *N* HCl	1 = no ppt. 40 mg. Pb in 10 cc. forms ppt. on shaking and letting stand.
	$Pb(NO_3)_2 + H_2SO_4$	add 0.5 cc. 0.5 *N* H_2SO_4	5 = slight ppt. forms shortly.
	$Pb(NO_3)_2 + KI$	add 0.5 cc. 0.5 *N* KI	6 = slight ppt. forms shortly. 7 = clear.
	$Pb(NO_3)_2 + K_2Cr_2O_7$	add 0.5 cc. 0.5 *N* $K_2Cr_2O_7$	9–12 = decreasing yellow cloudiness, 13 = clear.
	$Pb(NO_3)_2 + H_2S$	0.25 *N* HCl, pass in H_2S 0.5 min.	10 = slight stain, 14 = last visible tinge.
Hg (ic)	$Hg(NO_3)_2 + SnCl_2$	add 0.5 cc. 0.5 *N* $SnCl_2$	7 = last tinge of gray.
	$Hg(NO_3)_2 + Cu$	add small piece of clean copper wire, warm slightly, let stand 1 min.	5 = very faint silvery coating.
	$Hg(NO_3)_2 + H_2S$	0.25 *N* HCl, pass in H_2S 0.5 min.	8 = slight brown, 9 = very faint.
Bi	$Bi(NO_3)_3 + H_2S$	0.25 *N* HCl, pass in H_2S 0.5 min.	10 = faint tinge, 11 = doubtful.
	$Bi(NO_3)_3 + NH_4OH$	add 0.5 cc. 5 *N* NH_4OH	10 = slight ppt.
	$Bi(OH)_3 + Na_2SnO_2$	add 2–3 cc. 5 *N* NaOH to 1 cc. of $SnCl_2$ soln., pour reagent over ppt. of $Bi(OH)_3$ on filter	9 = distinct black, 10 = faint brown tinge, 11 = no visible effect.
	$Bi(NO_3)_3 + KI$	add 1 cc. 5 *N* HCl + 0.5 cc. 0.5 *N* KI	11 = last faint yellow.
	$Bi(NO_3)_3 + H_2O + HCl$	add 0.5 cc. 5 *N* HCl and look for white ppt. of BiOCl	7 = last opalescence.
Cu (ic)	$CuSO_4 + H_2S$	0.25 *N* HCl, pass in H_2S 0.5 min.	11 = faint brown color.
	Color of Cu^{++}		5 = last blue tinge.
	Color of $Cu(NH_3)_4^{++}$	add 2 cc. 5 *N* NH_4OH	8 = last blue tinge.
	$CuSO_4 + K_4Fe(CN)_6$	add 0.5 cc. 0.5 *N* $K_4Fe(CN)_6$	9 = last visible pink, 11 = last discoloration.
Cd	$CdSO_4 + H_2S$	0.25 *N* HCl, pass in H_2S 0.5 min.	9 = last yellowish white tinge.
	$Cd(NH_3)_4SO_4 + H_2S$	add 2 cc. 2 *N* NH_4Cl + 1 cc. 5 *N* NH_4OH, pass in H_2S 0.5 min.	6 = visible particles of ppt., 11 = last faint color.
	$Na_2Cd(CN)_4 + H_2S$	add 2 cc. 2 *N* NH_4Cl + 1 cc. 5 *N* NH_4OH + 3 cc. *N* NaCN, pass in H_2S 0.5 min.	6 = yellow particles, 10 = last milky yellow color.

TABLE 33. — *Continued*

Metal	Reaction	Special conditions	Effects observed in the tubes containing the lower concentrations of metal
Sn (ous)	$SnCl_2 + H_2S$	0.25 *N* HCl, pass in H_2S 0.5 min.	10 = last discoloration.
	$SnCl_2 + HgCl_2$	add 2 cc. 5 *N* HCl, 0.3 g. powd. Fe, warm, let stand 2 min., filter into 2 cc. 0.25 *N* $HgCl_2$, look for white ppt.	8 = visible ppt., 9 = faint test.
Sn (ic)	$SnCl_4 + H_2S$	0.25 *N* HCl, pass in H_2S 0.5 min.	9 = last yellow tinge.
Sb (ous)	$SbCl_3 + H_2S$	0.25 *N* HCl, pass in H_2S 0.5 min.	12 = last color.
	$SbCl_3 + Fe$	add 2 cc. 5 *N* HCl + iron wire, warm and look for black ppt. floating in soln.	4 = last definite ppt.
	$SbCl_3 + Sn$	place 2 drops of soln. on Ag coin, add bridge of Sn foil and look for stain on Ag after 0.5 min.	6 = distinct brown stain, 7 = doubtful.
	$SbCl_3 + H_2O$	note limit of white ppt. on diluting	5 = white ppt., 6 = slight opalescence, 7 = clear.
As (ous)	$H_3AsO_3 + H_2S$	0.25 *N* HCl, pass in H_2S 0.5 min.	12 = last tinge of color.
As (ic)	$H_3AsO_4 + H_2S$	2.5 *N* HCl, heat to boiling, pass in H_2S 0.5 min.	11 = last yellowish white color.
	$H_3AsO_4 + NH_4OH + MgCl_2$	add 2 cc. 5 *N* NH_4Cl, + 1 cc. 5 *N* NH_4OH, + 0.5 cc. 0.5 *M* $MgCl_2$, stir with glass rod	8 = faint crystalline ppt.
	$H_3AsO_4 + AgNO_3 + NH_4OH$	add 5 cc. 5 *N* HNO_3 + 2 cc. 0.5 *N* $AgNO_3$, shake, tilt test tube and pour in an upper layer of 2–3 cc. 5 *N* NH_4OH. Look for brown ring of Ag_3AsO_4 between layers	6 = definite brown ring, 7 = doubtful.
Fe (ous)	$FeSO_4 + K_3Fe(CN)_6$	add 1 cc. 5 *N* HCl, + 0.5 cc. 0.5 *M* $K_3Fe(CN)_6$	9 = faint blue color, 10 = visible change as compared with blank, 11 = same as blank.
Fe (ic)	Color of $FeCl_3$		6 = last yellow tinge.
	$FeCl_3 + NH_4OH$	add 2 cc. 2 *N* NH_4Cl, heat, add 0.5 cc. 5 *N* NH_4OH	8 = last flocculent ppt., 11 = last tinge of color.
	$FeCl_3 + KCNS$	add 1 cc. 5 *N* HCl + 0.5 cc. 0.5 *M* KCNS	11 = pink tinge, 13 = last visible tinge.
	$FeCl_3 + K_4Fe(CN)_6$	add 1 cc. 5 *N* HCl + 0.5 cc. 0.5 *M* $K_4Fe(CN)_6$	8 = deep blue color, 12 = light blue green, 13 = very faint. (Color must be judged rather promptly as blue color develops in a little while from decomposition of the reagent itself.)
Al	$AlCl_3 + NH_4OH$	add 2 cc. 2 *N* NH_4Cl, heat, add 0.5 cc. 5 *N* NH_4OH	5–6 = almost transparent gelatinous ppt., 7 = limit of immediate visibility, 8 = flocculates slightly after 20 min.

TABLE 33. — *Continued*

Metal	Reaction	Special conditions	Effects observed in the tubes containing the lower concentrations of metal
Al	$NaAlO_2 + NH_4Cl$	add 2 cc. 5 *N* NaOH, then 10 cc. 2 *N* NH_4Cl, heat, let stand 2-3 min.	7 = immediate opalescence in cold, 8-9 = visible on heating and short standing, 10 = doubtful.
	"Aluminon test."	dilute solns. as usual, add 5 cc. of the 0.1% reagent, + 5 cc. 3 *N* $NH_4C_2H_3O_2$, + 2 cc. 5 *N* NH_4OH	7-8 = immediate separation of red ppt., 9 = ppt. separates more slowly, 12 = faint red color visible, 13 = indistinguishable from blank.
Cr (ic)	Color of $CrCl_3$		5 = last definite color, 6 = doubtful.
	$CrCl_3 + NH_4OH$	add 2 cc. 2 *N* NH_4Cl, heat to near boiling, add 0.5 cc. 5 *N* NH_4OH	7 = visible ppt., 8 = very slight, 9 = doubtful.
	$CrO_2^- + H_2O_2$	add 1 cc. 5 *N* NaOH, + 0.5 cc. H_2O_2, boil, note color	8 = yellow color, 9 = very faint.
Cr (6)	Color of $Cr_2O_7^{--}$		9 = visible yellow color, 10 = faint, 11 = doubtful.
	$Cr_2O_7^{--} + H^+ + H_2O_2$	add 1 cc. 5 *N* H_2SO_4, + 0.5 cc. H_2O_2, note color	8 = strong blue color, 10 = faint, 11 = doubtful.
	$Cr_2O_7^{--} + BaCl_2$	add 0.5 cc. of 0.5 *N* $NaC_2H_3O_2$, + 0.5 cc. 0.5 *N* $BaCl_2$	7 = silky yellow-white ppt., 8-10 = opalescence.
	$Cr_2O_7^{--} + Pb(C_2H_3O_2)_2$	add 0.5 cc. of 0.5 *N* $NaC_2H_3O_2$, + 0.5 cc. 0.5 *N* $Pb(C_2H_3O_2)_2$	10 = slight ppt., 11-13 = faint yellow color and slight opalescence.
Zn	$Zn(NH_3)_4SO_4 + H_2S$	add 2 cc. 2 *N* NH_4Cl + 0.5 cc. 5 *N* $NH_4OH + H_2S$ (15 seconds)	9 = faint milky soln., 10 = doubtful.
	$ZnO_2^{--} + H_2S$	add 2 cc. 5 *N* NaOH + H_2S (15 seconds)	7 = becomes milky while H_2S is being passed in. 8-11 = decreasing opalescence on short standing.
	$ZnSO_4 + K_4Fe(CN)_6$	add 0.5 cc. 0.5 *M* $K_4Fe(CN)_6$	7 = immediate pptn., 8-12 = milky appearance, develops a little slowly (but seen by holding the test tube in the light and looking through it at a dark background).
	$ZnSO_4 + H_2S$	add 2 cc. 3 *N* $NH_4C_2H_3O_2$ + H_2S (15 seconds)	7 = visible pptn. while treating with H_2S, 8-9 = faint milky soln. at end of treatment, 10 = very faint.
	$ZnSO_4 + NH_4OH$	add 2 cc. 2 *N* NH_4Cl + 0.5 cc. 5 *N* NH_4OH	1 = white ppt., other solns. = no visible action.
Mn (ous)	$MnSO_4 + NH_4OH + H_2S$	add 2 cc. 2 *N* NH_4Cl + 0.5 cc. 5 *N* $NH_4OH + H_2S$ (15 seconds)	9 = becomes cloudy while treating with H_2S, 10-11 = cloudy after short standing, 12 = clear.
	$MnSO_4 + NH_4OH$	add 1 cc. 5 *N* NH_4OH	6-11 = decreasing brown ppt., 12 = slowly develops brown tinge.
	$MnSO_4+NH_4Cl+NH_4OH$	add 2 cc. 2 *N* NH_4Cl + 1 cc. 5 *N* NH_4OH	1-4 = white ppt., turning brown, 5 = slowly develops a tan color.
	$MnSO_4+Pb_3O_4+HNO_3$	add 5 cc. 5 *N* HNO_3 + 0.3 g. Pb_3O_4, boil, let settle	1-2 = incomplete oxidation, 11 = visible red color, 12 = doubtful.
	$MnSO_4+AgNO_3+K_2S_2O_8$	add 5 cc. 5 *N* HNO_3 + 5 drops 0.25 *N* $AgNO_3$ + 0.3 g. $(NH_4)_2S_2O_8$, boil, note color	1-6 = incomplete oxidation, 7-12 = color decreased from reddish purple to faint pink.

TABLE 33. — *Continued*

Metal	Reaction	Special conditions	Effects observed in the tubes containing the lower concentrations of metal
Mn (7)	Color of MnO_4^-		12–13 = very faint, 14 = clear.
Co	Color of Co^{++}		4 = faint pink, 5 = doubtful.
	Color of $Co(NH_3)_4^{++}$	add 2 cc. 2 *N* NH_4Cl + 0.5 cc. 5 *N* NH_4OH	5 = light pink, 6 = very faint.
	$Co(NH_3)_4Cl_2 + H_2S$	add 2 cc. 2 *N* NH_4Cl + 0.5 cc. 5 *N* NH_4OH + H_2S (15 seconds)	13 = last brownish tinge.
	$CoCl_2 + NH_4OH$	add 2 cc. 2 *N* NH_4Cl + 0.5 cc. 5 *N* NH_4OH	1–2 = blue green ppt., 3 = slightly cloudy, 4 = clear.
	$CoCl_2 + NH_4CNS$	add 2 g. NH_4CNS + 2 cc. amyl alcohol, shake and let stand	9 = distinct blue color in alcohol layer, 10 = faint.
	$CoCl_2 + NaHCO_3 + H_2O_2$	add 2 g. $NaHCO_3$ + 0.5 cc. H_2O_2, shake and let stand	9 = distinct green color, 10 = doubtful.
	Color of anhydrous $CoCl_2$	evaporate to dryness in casserole and heat residue gently. Note blue color of residue	12 = blue color readily visible.
	$CoCl_2 + HCl$	treat residue from the preceding experiment with 5 cc. of conc. HCl and note color of soln.	9–11 = blue green color decreasing in depth, 12 = barely visible color.
Ni	Color of Ni^{++}		2 = light green, 3 = doubtful.
	Color of $Ni(NH_3)_4^{++}$	add 2 cc. 2 *N* NH_4Cl + 0.5 cc. 5 *N* NH_4OH	1–4 = blue color, 5 = faint, 6 = doubtful.
	$Ni(NH_3)_4Cl_2 + H_2S$	add 2 cc. 2 *N* NH_4Cl + 0.5 cc. 5 *N* NH_4OH + H_2S (15 seconds)	13 = faint brown color.
	$NiCl_2 + NH_4OH$	add 2 cc. 2 *N* NH_4Cl + 0.5 cc. 5 *N* NH_4OH	1 = no ppt. (no ppt. with 80 mg. of Ni).
	$NiCl_2 + NH_4OH + C_4H_8N_2O_2$	add 2 cc. 2 *N* NH_4Cl + 1 cc. 5 *N* NH_4OH + 1 cc. of 1% soln. of $C_4H_8N_2O_2$ in 95% alcohol	9 = immediate red ppt., 10–11 = tan, turning pink after several minutes.
Ba	$BaCl_2 + NH_4Cl + NH_4OH + (NH_4)_2CO_3$	add 2 cc. 2 *N* NH_4Cl + 1 cc. 5 *N* NH_4OH, heat to near b.p. + 0.5 cc. of 0.5 *M* $(NH_4)_2CO_3$	1–2 = immediate pptn., 3 = slight, 4 = very faint. (On rinsing tubes later, granular particles were found on walls of test tubes in 4 and 5.)
	$BaCl_2 + NH_4OH + (NH_4)_2CO_3$	add 1 cc. 5 *N* NH_4OH, heat to near b.p. + 0.5 cc. of 0.5 *M* $(NH_4)_2CO_3$	6 = ready pptn., 7 = faint, 8 = clear.
	$BaCl_2 + (NH_4)_2SO_4$	add 0.5 cc. 0.5 *M* $(NH_4)_2SO_4$	11 = faint ppt. (ppt. = silky in appearance from 7 to 11).
	$BaCl_2 + K_2Cr_2O_7$	add 0.5 cc. 0.5 *M* $K_2Cr_2O_7$	1–4 = immediate pptn., 5–6 = ppt. forms slowly.
	$BaCl_2 + NH_4C_2H_3O_2 + K_2Cr_2O_7$	add 0.5 cc. 3 *N* $NH_4C_2H_3O_2$ + 0.5 cc. 0.5 *M* $K_2Cr_2O_7$	8 = immediate pptn., 9 = slow.
	$BaCl_2 + (NH_4)_2C_2O_4$	add 0.5 cc. 0.5 *M* $(NH_4)_2C_2O_4$	2 = immediate granular ppt., 3 = slow pptn., 4 = none in 15 min.
	$BaCl_2 + NH_4Cl + NH_4OH + (NH_4)_2HPO_4$	add 2 cc. 5 *N* NH_4Cl + 1 cc. 5 *N* NH_4OH + 1 cc. 0.5 *M* $(NH_4)_2HPO_4$	3 = gelatinous ppt. turning granular, 4 = ppts. slowly on heating.
	$BaCl_2$ flame test	clean Pt wire, dip in solution and hold in Bunsen flame	1 = distinct green flame, 2 = faint, 3 = doubtful.

TABLE 33. — *Continued*

Metal	Reaction	Special conditions	Effects observed in the tubes containing the lower concentrations of metal
Ba	Flame test on $BaSO_4$ + HCl	add 2 cc. of 0.1 *M* $(NH_4)_2SO_4$, filter, wash, spread tip of filter out on watch glass, add 2 drops of 5 *N* HCl and try flame test with Pt wire	5 = strong green flame, 6 = moderate, 7 = occasional green flashes, 8 = blank.
Sr	$SrCl_2 + NH_4Cl + NH_4OH + (NH_4)_2CO_3$	add 2 cc. 2 *N* NH_4Cl + 1 cc. 5 *N* NH_4OH, heat to near b.p. + 0.5 cc. of 0.5 *M* $(NH_4)_2CO_3$	4–5 = slight ppt., 6 = doubtful.
	$SrCl_2 + NH_4OH + (NH_4)_2CO_3$	add 1 cc. 5 *N* NH_4OH, heat to near b.p. + 0.5 cc. of 0.5 *M* $(NH_4)_2CO_3$	9 = visible ppt., 10 = very faint.
	$SrCl_2 + (NH_4)_2SO_4$	add 0.5 cc. of 0.5 *M* $(NH_4)_2SO_4$, heat	5 = ppts. slightly, 6 = very faint.
	$SrCl_2 + CaSO_4$	add 10 cc. sat. $CaSO_4$, boil, let stand 5 minutes	3 = slight ppt., 4 = faint ppt., forms only after several hours.
	$SrCl_2 + (NH_4)_2C_2O_4$	add 0.5 cc. 0.5 *M* $(NH_4)_2C_2O_4$ and heat	3–6 = cryst. ppt., 7 = slight ppt.
	$SrCl_2 + K_2Cr_2O_7 + NH_4C_2H_3O_2$	add 0.5 cc. 3 *N* $NH_4C_2H_3O_2$ + 0.5 cc. 0.5 *M* $K_2Cr_2O_7$	1 = no ppt. (no ppt. with 100 mg Sr).
	$SrCl_2 + NH_4Cl + NH_4OH + (NH_4)_2HPO_4$	add 2 cc. 5 *N* NH_4Cl + 1 cc. 5 *N* NH_4OH + 1 cc. 0.5 *M* $(NH_4)_2HPO_4$	4 = opalescent, changing to fine ppt. on heating, 5 = slight ppt. on heating, 6 = clear.
	$SrCl_2$ flame test	clean Pt wire, dip in soln., and hold in Bunsen flame	4 = distinct color, 5–7 = decreasing color (showing especially at top when wire is heated in middle and drawn slowly to tip). 8 = occasional flashes.
	Flame test on $SrSO_4$	add 2 cc. 0.5 *M* $(NH_4)_2SO_4$, boil, let stand 5 min., filter, wash, spread tip of filter out on watch glass, add 2 drops of 5 *N* HCl, and try flame test with Pt wire	6 = strong crimson flame (6 = last to show ppt., 7 was filtered and paper tested, but results were negative).
Ca	$CaCl_2 + NH_4Cl + NH_4OH + (NH_4)_2CO_3$	add 2 cc. 2 *N* NH_4Cl + 1 cc. 5 *N* NH_4OH, heat to near b.p. + 0.5 cc. 0.5 *M* $(NH_4)_2CO_3$	5 = slight ppt., 6 = doubtful.
	$CaCl_2 + NH_4OH + (NH_4)_2CO_3$	add 1 cc. 5 *N* NH_4OH, heat to near b.p. + 0.5 cc. of 0.5 *M* $(NH_4)_2CO_3$	9 = visible ppt., 10 = faint, 11 = clear.
	$CaCl_2 + (NH_4)_2SO_4$	add 0.5 cc. of 0.5 *M* $(NH_4)_2SO_4$ and heat	1 = no ppt. (with 1 cc. $(NH_4)_2SO_4$ a slight ppt. forms fairly readily).
	$CaCl_2 + (NH_4)_2C_2O_4$	add 0.5 cc. of 0.5 *M* $(NH_4)_2C_2O_4$, heat if ppt. does not form immediately	5 = immediate pptn., 6–8 = slower, 9 = visible pptn. on heating, 10 = very faint.
	$CaCl_2 + K_4Fe(CN)_6$	add 0.5 cc. of 0.5 *M* $K_4Fe(CN)_6$, heat if ppt. does not form immediately	1 = granular ppt. forms slowly. (On adding 2 cc. of 5 *N* NH_4Cl and heating, ppts. form in 4–7, settling very slowly from opalescent soln. Reagents themselves show opalescence on heating.)
	$CaCl_2 + NH_4Cl + NH_4OH + (NH_4)_2HPO_4$	add 2 cc. of 5 *N* NH_4Cl + 1 cc. 5 *N* NH_4OH + 0.5 cc. 0.5 *M* $(NH_4)_2HPO_4$	6–7 = slight ppt., 8 = visible on heating.

TABLE 33. — *Continued*

Metal	Reaction	Special conditions	Effects observed in the tubes containing the lower concentrations of metal
Ca	$CaCl_2$ flame test	clean Pt wire, dip in soln., and hold in Bunsen flame	5 = faint reddish tinge as wire is inserted, 6–7 = decreasing flashes of color at tip of wire as wire is drawn slowly through flame, 8 = blank.
	Flame test on CaC_2O_4	heat to b.p., add 1 cc. of 0.5 *M* $(NH_4)_2C_2O_4$, let stand 5 min., filter, wash, spread tip of filter out on watch glass, add 2 drops of 5 *N* HCl, and try flame test with Pt wire	7 = strong Ca flame, 8 = distinct, 9 = faint.
Mg	$MgCl_2+NH_4Cl+NH_4OH$	add 2 cc 2 *N* NH_4Cl + 1 cc. 5 *N* NH_4OH	1 = no ppt. (no ppt. with 160 mg. of Mg.)
	$MgCl_2 + NH_4OH$	add 1 cc. of 5 *N* NH_4OH	4–5 = visible ppt., 6 = clear.
	$MgCl_2 + NH_4Cl + NH_4OH + (NH_4)_2HPO_4$	add 2 cc. 2 *N* NH_4Cl + 1 cc. 5 *N* NH_4OH + 0.5 cc. 0.5 *M* $(NH_4)_2HPO_4$, stir with glass rod	6 = immediate pptn., 7–9 = ready pptn. on stirring, 10 = faint.
	$MgCl_2 + NH_4Cl + NH_4OH + (NH_4)_2CO_3$	add 2 cc. 2 *N* NH_4Cl + 1 cc. 5 *N* NH_4OH, heat nearly to b.p. + 0.5 cc. 0.5 *M* $(NH_4)_2CO_3$	1 = no ppt. (no ppt. with 40 mg. of Mg.)
	$MgCl_2 + NH_4Cl + (NH_4)_2C_2O_4$	add 2 cc. 2 *N* NH_4Cl + 0.5 cc. of 0.5 *M* $(NH_4)_2C_2O_4$, and heat	1 = no ppt. (no ppt. with 80 mg. of Mg.)
NH_4^+	NH_4Cl + NaOH (odor-cold)	add 1 cc. 5 *N* NaOH, shake, note odor	1 = distinct, 2 = faint, 3 = not recognized.
	NH_4Cl + NaOH (odor-hot)	add 1 cc. 5 *N* NaOH, heat to near b.p., note odor	3 = strong, 4–6 recognizable, 7 = doubtful.
	NH_4Cl + NaOH (litmus test)	add 1 cc. of 5 *N* NaOH, shake, place strip of moist red litmus across mouth of t.t. If color does not change remove test paper, heat soln., and replace litmus paper	1 = turns blue promptly in the cold 2 = turns blue slowly in the cold. 3–4 = turns blue promptly in the hot. 5–7 = turns blue slowly in the hot. 8 = visible change showed over part of the exposed surface.
	NH_4Cl + NaOH ($MnSO_4$ + H_2O_2 test paper)	add 1 cc. of 5 *N* NaOH, heat to near b.p., cover with test paper (1 cc. $MnSO_4$ + 1 cc. H_2O_2. 1 drop on filter paper)	4 = brown stain develops promptly, 5–7 = decreasing stain appears more slowly, 8 = blank.
	NH_4Cl + NaOH Nessler's Reagent test	add 1 cc. of 5 *N* NaOH + 2 cc. of 0.05 *M* K_2HgI_4	7 = reddish brown ppt., 8–12 = cloudiness decreasing to yellow-brown solution easily distinguished from "blank."
K	KCl flame test	flame observed in slightly darkened room through "Co-glass" of methyl violet screen. Pt wire used	4 = reddish violet flash of color, visible every time, 5–6 = fainter flashes, visible occasionally.
Na	NaCl flame test	flame observed in slightly darkened room	Adjacent solutions were distinguishable from each other by the depth and duration of the yellow color, varying from brilliant yellow, lasting several seconds in 1, to a faint yellow lasting 0.1–0.2 seconds in 8, 8 = faint test, recognizable as compared with dist. water.

PART II

THE METALS

THE SILVER GROUP (FIRST GROUP)

LEAD, MERCURY (OUS), SILVER, (THALLIUM)

§57. Lead (Anglo-Sax. lead) (Plumbum). Pb = 207.22. Atomic No. 82. Valence 2 and 4. Discovery prehistoric.

1. Physical Properties. — *Density*, 11.48 ± 0.03 (X-ray method);[1] 11.38 (Immersion method);[2] melting point, 327.4°;[3] *boiling point*, 1613° (calc.).[4] Lead boils rapidly before the oxy-hydrogen blowpipe, but cannot be distilled like zinc *per se* in closed vessels. In the absence of air, lead is not sensibly volatilized below a white heat.

Pure lead is almost white, soft, malleable, and slightly ductile; it tarnishes in air forming a film of oxide. The presence of traces of most other metals makes the lead appreciably harder. It is a poor conductor of heat and electricity. It forms alloys with many metals: lead and tin in various proportions form solder and pewter; lead and arsenic (0.5%) form shot metal; lead and antimony (20–25%) form type metal; lead, bismuth, tin and cadium form an alloy melting as low as 65°; white metal consists of varying proportions of lead, antimony, tin and sometimes copper.

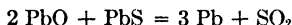
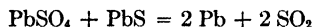
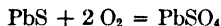
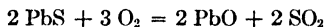
2. Occurrence. — The most abundant lead ore is galena, PbS. Lead also occurs as cerrusite, $PbCO_3$; anglesite, $PbSO_4$; pyromorphite, $Pb_5Cl(PO_4)_3$; and in many other minerals of minor importance. The United States (chiefly Missouri, Idaho and Utah) produces about one half of the world's supply. Mexico, Spain and Roumania each produce about one tenth. The total annual output is approximately 1,300,000 tons.

3. Preparation. — (a) The ore, e.g., galena, is roasted in air, thus forming variable quantities of $PbSO_4$ and PbO mixed with unchanged PbS. The air is then excluded and the temperature raised. The sulfur of the sulfide reduces both the PbO and the $PbSO_4$, SO_2 being formed:[5]

$$2\,PbS + 3\,O_2 = 2\,PbO + 2\,SO_2$$

$$PbS + 2\,O_2 = PbSO_4$$

$$PbSO_4 + PbS = 2\,Pb + 2\,SO_2$$

$$2\,PbO + PbS = 3\,Pb + SO_2$$

(b) Similar to the first method except that some form of carbon is used to aid in the reduction. (c) Galena is reduced by fusing with scrap iron: $PbS + Fe = Pb + FeS$. Frequently these methods are combined or varied according to the other constituents of the ore. Concentration by flotation is, of course, the first step when necessary.

4. Oxides. — (Pb_2O), PbO, Pb_3O_4, PbO_2, Pb_2O_3, $Pb_5O_7 \cdot 3H_2O$.

a. Lead suboxide, Pb_2O, is obtained as a black powder by heating PbC_2O_4 below 300° in the absence of air:

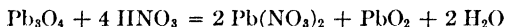
$$2\,PbC_2O_4 = Pb_2O + CO + CO_2$$

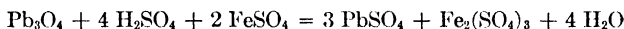
[1] Davey, *Phys. Rev.*, [2] **25**, 753 (1925).
[2] Richards and Wadsworth, *J. Am. Ch. Soc.* **38**, 225 (1916).
[3] B. Stds. *Cir.* **35**, Guertler and Pirani, *Z. Metallkunde*, **11**, 1 (1919).
[4] Van Liempt, *Z. anorg. allgem. Ch.*, **114**, 105 (1920).
[5] Evans, IV, 260–73.

It is unstable, changing to Pb and PbO. Some investigators have questioned the existence of this oxide.[1]

b. Lead monoxide, PbO,[2] is formed by igniting (in the presence of air): Pb, PbO_2, Pb_3O_4, $Pb(OH)_2$, $PbCO_3$, PbC_2O_4 or $Pb(NO_3)_2$. The temperature largely determines the color and form of the product, litharge being obtained in the higher ranges. It melts at 888°[3] and is sensibly volatile at temperatures below 1000°.[4]

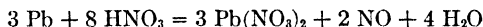
c. Trilead tetroxide, Pb_3O_4, red lead or minium, is a bright red powder formed by heating PbO at 400° for several hours, preferably with stirring to insure adequate contact with the air. At higher temperatures it decomposes with evolution of oxygen. Strong non-reducing acids, e.g., HNO_3, H_2SO_4, and $HClO_3$, convert it into a lead salt and PbO_2:

$$Pb_3O_4 + 4\ HNO_3 = 2\ Pb(NO_3)_2 + PbO_2 + 2\ H_2O$$

Reducing acids (hydracids, etc.) or non-reducing acids plus reducing agents capable of reducing the PbO_2 (see 5, *b*) dissolve red lead without evolution of oxygen:

$$Pb_3O_4 + 4\ H_2SO_4 + 2\ FeSO_4 = 3\ PbSO_4 + Fe_2(SO_4)_3 + 4\ H_2O$$

The valences of lead in Pb_3O_4 are two and four as shown by the formula Pb_2PbO_4 to which the name plumbus orthoplumbate is given.[5]

d. Lead dioxide or *peroxide*, PbO_2, a dark brown powder, is formed: (a) by fusion of PbO with chlorates or nitrates; (b) by treating bivalent lead in alkaline solution with oxidizing agents, as halogens, H_2O_2, $KMnO_4$, NaClO, etc.; (c) by treating Pb_3O_4 with non-reducing acids (4, *c*); (d) by anodic oxidation of bivalent lead. Ignition at lower temperatures forms Pb_3O_4; above a red heat, PbO, oxygen being evolved. Lead dioxide dissolves in acids under the same conditions as Pb_3O_4 (5, *b*). The dioxide is a powerful oxidizing agent, one of the strongest known. Digested with NH_4OH some nitrate is formed; triturated with small amounts of sulfur, tartaric acid or sugar the mixture takes fire; with phosphorus it detonates.

5. Solubilities. — *a. Metal.* — Dilute HNO_3 (1 : 1) is the best of the common solvents for metallic lead:[6]

$$3\ Pb + 8\ HNO_3 = 3\ Pb(NO_3)_2 + 2\ NO + 4\ H_2O$$

The presence of nitrite hastens the action. Concentrated HNO_3 is a less effective solvent because lead nitrate is insoluble in this acid and forms a protective film on the metal preventing further action. Dilute H_2SO_4 has slight action; the concentrated acid is almost without effect in the cold but when hot it slowly changes the metal to the sulfate with evolution of SO_2. A portion of the salt dissolves in the acid but precipitates on the addition of water. HCl attacks lead slowly, hydrogen being evolved; the chloride formed dissolves to an extent dependent upon the temperature and concentration of the solvent. F, Cl, and Br attack lead slowly; I has no effect. Alloys of lead are best dissolved by first treating with HNO_3.[7] If a white residue is left it is washed with water and, if not dissolved, is treated with HCl in which it will usually be soluble.

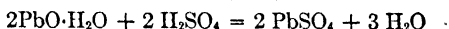
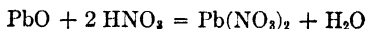
The chemical properties of lead present some curious contrasts. The metal resists the action of H_2SO_4 or HCl much better than iron, zinc or tin, yet it is readily attacked by weak organic acids; it slowly dissolves even in water, and is quickly corroded by moist air.[8]

b. Oxides. — Lead suboxide, Pb_2O, is decomposed by heat, acids or alkalis into Pb and PbO.

[1] See, however, Ferrari, *Gazz. ch. ital.*, **56**, 630 (1926).
[2] The yellowish variety is called massicot; the reddish, litharge.
[3] Cooper, *et al.*, *Ber.*, **42**, 3993 (1909).
[4] Döltz and Graumann, *Chem. Zentr.*, **78**, II, 442.
[5] Grube, *Z. Elektroch.*, **28**, 273 (1922).
[6] Lunge and Schmidt, *Z. angew. Ch.*, **5**, 666 (1892).
[7] HCl with HNO_3 or $NaClO_3$ is desirable in the case of some Pb alloys.
[8] Mellor, VII, 561.

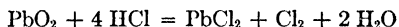
Lead monoxide, PbO, and the hydroxides, $2PbO \cdot H_2O$ and $3PbO \cdot H_2O$, react readily with acids forming the corresponding salts:

$$PbO + 2\,HNO_3 = Pb(NO_3)_2 + H_2O$$

$$2PbO \cdot H_2O + 2\,H_2SO_4 = 2\,PbSO_4 + 3\,H_2O$$

The oxide and hydroxide are soluble in water to the extent of 0.85 g. per liter at 25°,[1] the resulting solutions reacting alkaline. They are soluble in the fixed alkali and alkaline earth hydroxides forming plumbites; in certain salts, e.g., chlorides, acetates, citrates, tartrates, etc.; very soluble in $Pb(C_2H_3O_2)_2$ forming basic lead acetate.

Trilead tetroxide, Pb_3O_4, although insoluble in water, is attacked by nearly all acids in the cold forming the corresponding bivalent salt and lead dioxide. It may be dissolved by any of the reagents that are effective for the dioxide (q.v.).

Lead dioxide, PbO_2, is insoluble in water or HNO_3. It is dissolved by the halogen hydracids with liberation of the halogen and formation of the corresponding lead halide:

$$PbO_2 + 4\,HCl = PbCl_2 + Cl_2 + 2\,H_2O$$

It is attacked by hot, concentrated H_2SO_4 forming the sulfate and liberating oxygen. The presence of a reducing agent, e.g., free metal, alcohol, formaldehyde, oxalic acid, H_2O_2, etc., greatly facilitates the solution of red lead or lead dioxide in acids. HNO_3 does not dissolve PbO_2 but if a few drops of H_2O_2 be added solution takes place readily upon warming. It reacts with certain acids in the cold forming salts of quadrivalent lead, e.g., glacial acetic acid forms $Pb(C_2H_3O_2)_4$.[2] These salts are very unstable, decomposing to give the bivalent salt when warmed.[3] The peroxide is slowly soluble in the fixed alkalis forming plumbates:[4] $PbO_2 + 2\,NaOH = Na_2PbO_3 + H_2O$.

c. Salts. — A number of sub-salts, as PbCl, have been prepared and some of their properties studied;[5] quadrivalent salts have also been reported.[6] Among the bivalent salts the carbonate, borate, chromate, cyanide, ferrocyanide, iodate, oxalate, phosphate, sulfide, sulfite and tannate are insoluble in water. The sulfate is soluble to the extent of 0.042 g. per liter at room temperature;[7] more soluble in the presence of HNO_3 or HCl; insoluble in alcohol even when dilute; slightly soluble in concentrated H_2SO_4, the solubility varying markedly with the percentage of acid;[8] less soluble in dilute H_2SO_4 than in water;[9] more soluble in HCl than in HNO_3, although the solubility increases slightly with the concentration of the solvent;[10] transposed and dissolved by excess of HCl,

[1] Cumming, *Trans. Faraday Soc.*, **2**, 211 (1907).
[2] Hutchinson and Pollard, *J. Ch. Soc.*, **69**, 212 (1896).
[3] Fisher, *Ibid.*, **35**, 282 (1879).
[4] Simon, *Z. anorg. allgem. Ch.*, **177**, 109 (1928).
See, however, Glasstone, *J. Ch. Soc.*, **121**, 1463 and 1478 (1922).
[5] Denham, *Ibid.*, **111**, 29 (1917); **113**, 249 (1918); **115**, 109 (1919).
[6] Chloride: Gutbier and Wissmüller, *J. prakt. Ch.*, **90**, 491 (1914); Krause, *Ber.*, **57B**, 318 (1924).
Nitrate: Chwala and Colle, *Z. anal. Ch.*, **50**, 241 (1911).
Sulfate: Elbs and Fischer, *Z. Elektroch.*, **7**, 343 (1900–1).
[7] Barre, *Ann. ch. phys.*, [8] **24**, 190 (1911).
Huybrechts and Ramelot, *Bull. soc. ch. Belg.*, **36**, 239–60 (1927), give 0.034 g. per liter.
[8] Ditz and Kanhäuser, *Z. anorg. allgem. Ch.*, **98**, 128 (1916).
[9] In 0.01 *N* H_2SO_4 the solubility is 0.0055 g. per liter at 18°.
[10] Beck and Stegmüller, *Arb. kais. Gesundh.*, **34**, 446 (1910); cf. Smith, p. 60.

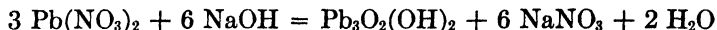
HBr or HI; insoluble in HF; almost completely transposed to the nitrate by standing several days in cold, concentrated HNO_3; soluble in ammonium chloride, nitrate, acetate,[1] tartrate and citrate, and not readily precipitated from these solutions by NH_4OH or a sulfate; soluble in aqueous NaOH, especially on warming; converted to PbO by concentrated NaOH (10 *N*).[2] The oxalate is soluble in water to the extent of 0.0016 g. per liter at 18°;[3] insoluble in alcohol. The ferricyanide is slightly soluble. The halides are slightly soluble in cold water; the change with temperature is indicated below:[4]

	$PbCl_2$ g./l.	$PbBr_2$ g./l.	PbI_2 g./l.
25°	10.8	9.85	0.77
100°	33.4	47.7	4.4

The solubility of $PbCl_2$ in water is affected by the addition of other chlorides, falling to a minimum (repression of solubility by common ion) and then rising again as the concentration of chloride ion is increased (formation of the complex ion $PbCl_4^{--}$). Minimum solubilities are found in 2.9 *N* HCl, 1.2 *N* KCl, and 1.5 *N* NH_4Cl;[5] in the first case the amount dissolved is about one gram per liter. The chloride is more soluble in HNO_3 than in water. The chloride, bromide and iodide are insoluble in alcohol. The iodide is moderately soluble in solutions of alkali iodides; it is decomposed by ether. The basic acetates are soluble in the absence of carbonic acid. The basic nitrates are slightly soluble and are precipitated on adding KNO_3 to a solution of basic lead acetate.

The slight solubility of $PbCl_2$ in cold, dilute HCl makes it possible to precipitate most of the lead (see above) in the first group; while its solubility in hot water permits its separation from the other chlorides of that group. Any lead not removed in the first group is precipitated as the sulfide in the second group, separated from Bi, Cu, and Cd as the sulfate and identified as the chromate.

6. Reactions. — *a*. Fixed alkali hydroxides precipitate, from solutions of lead salts, hydrated lead oxide, $Pb_3O_2(OH)_2$:[6]

$$3\ Pb(NO_3)_2 + 6\ NaOH = Pb_3O_2(OH)_2 + 6\ NaNO_3 + 2\ H_2O$$

[1] Fox, *J. Ch. Soc.* (Proc.), **23**, 199 (1907); *Ibid.* (Trans.), **95**, 878 (1909).

[2] Kohlschütter and Roesti, *Ber.*, **56**, 287 (1923).

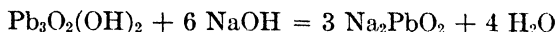
[3] Prud'homme, *J. ch. phys.*, **9**, 519 (1911).

[4] Herz and Hellebrandt, *Z. anorg. allgem. Ch.*, **130**, 188 (1923); Lichty, *J. Am. Ch. Soc.*, **25**, 469 (1903).

[5] Kendall and Sloan, *J. Am. Ch. Soc.*, **47**, 2310 (1925), state that minimum solubility for HCl and NH_4Cl is at about 1 *N*, for KCl at 1.2 *N*. Also, the minimum solubility in HCl is 1.3 g./l.

[6] Pleissner, *Arb. kais. Gesundh.*, **26**, 398 (1907).

The exact composition, however, is variable depending upon the temperature and concentration of the reactants.[1] The precipitate is white, soluble[2] in excess of the reagent forming plumbite (distinction from Ag, Hg, Bi, Cu and Cd):

$$Pb_3O_2(OH)_2 + 6\ NaOH = 3\ Na_2PbO_2 + 4\ H_2O$$

In lower concentrations of alkali the product formed appears to be of the type $MHPbO_2$, while in concentrated alkali there is evidence for the formation of M_2PbO_2.[3] There is apparently no ammonium plumbite. Sodium plumbate is obtained by fusing PbO or PbO_2 with an excess of NaOH in a silver crucible.

Ammonium hydroxide precipitates white basic salts, insoluble in water and in excess of the reagent (distinction from Ag, Cu and Cd); with the chloride the precipitate is $3PbO \cdot PbCl_2 \cdot H_2O$ (probably variable); with the nitrate, $5PbO \cdot Pb(NO_3)_2 \cdot H_2O$.[4] Excess of NH_4OH (free from carbonate) gives no precipitate with the acetate, in solutions of ordinary strength, due to the low concentration of both lead and hydroxyl ions.

Alkali carbonates and bicarbonates precipitate normal lead carbonate in the cold, basic lead carbonate when hot, the composition of which varies with conditions of precipitation but is chiefly $Pb_3(OH)_2\ (CO_3)_2$.[5] Solutions of lead salts when boiled with freshly precipitated $BaCO_3$ are completely precipitated.

b. Oxalic acid and alkali oxalates precipitate lead oxalate, PbC_2O_4, white, from solutions of lead salts; soluble in HNO_3, alkali oxalates and hot NH_4Cl; insoluble in $HC_2H_3O_2$.[6] Since lead acetate is a slightly ionized compound many of the insoluble compounds of lead dissolve in solutions of acetates (not acetic acid).

A solution of $Pb(C_2H_3O_2)_2$ precipitates a large number (and a solution of the subacetate a still larger number) of organic acids, color substances, resins, gums, etc. Indeed it is a rule, with few exceptions, that lead subacetate removes organic acids (not formic, acetic, butyric, valeric, or lactic); hence the importance of this reagent in certain phases of organic analysis.

Tannic acid precipitates lead incompletely from solutions of the acetate or nitrate, as yellow-gray lead tannate, soluble in acids.

[1] Glasstone, *J. Ch. Soc.*, **119**, 1689, 1914 (1921); **121**, 58 (1922).

[2] Nearly all salts of lead are soluble in the fixed alkali hydroxides, PbS being almost the only notable exception.

[3] Bert and Austerweil, *Z. Elektroch.*, **13**, 165 (1907).
Müller, *et al.*, *Z. physik. Ch.*, **114**, 129 (1924).

[4] Strömholm, *Z. anorg. allgem. Ch.*, **38**, 444 (1904).

[5] Salvadori, *Gazz. ch. ital.*, **34**, I, 87 (1904).
Altmann, *Z. anorg. allgem. Ch.*, **52**, 225 (1907).
Hawley, *J. Phys. Ch.*, **10**, 654 (1906).
Euston, *Ind. Eng. Ch.*, **6**, 202, 382 (1914).

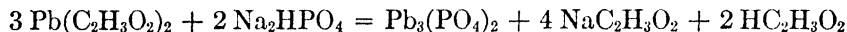
[6] Weinland, *Z. angew. Ch.*, **34**, *Aufsatzteil*, 354 (1921).

Soluble cyanides precipitate lead cyanide, $Pb(CN)_2$, (lead acetate gives $Pb_3O_2(CN)_2$) white, sparingly soluble in a large excess of the reagent; reprecipitated on boiling.[1] Potassium ferrocyanide precipitates lead ferrocyanide, $Pb_2Fe(CN)_6$, white, insoluble in water or dilute acids. A freshly prepared solution of $K_3Fe(CN)_6$ gives no visible action with $Pb(C_2H_3O_2)_2$.[2] Subsequent addition of NH_4OH causes the formation of a reddish-brown precipitate.

Solutions of lead salts yield, with NH_4CNS, white lead thiocyanate, $Pb(CNS)_2$, soluble in excess of the reagent and in HNO_3.

c. Lead nitrate is readily soluble in water and reacts with the oxide to form the basic nitrate, which may also be obtained by treating lead acetate with KNO_3.[3] While many basic nitrates of lead have been reported it is probable that some are mixtures rather than definite chemical compounds. The solubility of lead nitrate is greatly increased by the presence of the alkali or alkaline earth nitrates, a complex ion being formed.[4]

d. The higher oxides of lead are all reduced by H_3PO_2, lead phosphate being formed. PbO gives $Pb(H_2PO_2)_2$. The basic, normal, and acid phosphites of lead have been studied.[5] All are white and soluble in dilute acid (not acetic). Sodium orthophosphate, Na_2HPO_4,[6] precipitates from solutions of lead acetate or nitrate, normal lead phosphate, $Pb_3(PO_4)_2$:

$$3\,Pb(C_2H_3O_2)_2 + 2\,Na_2HPO_4 = Pb_3(PO_4)_2 + 4\,NaC_2H_3O_2 + 2\,HC_2H_3O_2$$

white, slightly soluble in $HC_2H_3O_2$; soluble in HNO_3 and the fixed alkalis; converted to PbI_2 by KI. The pyrophosphate, $Pb_2P_2O_7$, white, amorphous, is obtained upon treating the solution of a lead salt with $Na_4P_2O_7$. The precipitate is soluble in excess of the reagent, dilute acids and NaOH; insoluble in NH_4OH, $HC_2H_3O_2$ and H_2SO_3 (probably transposed by the latter). Lead metaphosphate (there are several forms), white, crystalline, is obtained by the action of $NaPO_3$ upon lead nitrate in excess. The product is insoluble in water and readily decomposed by acids.

e. Hydrosulfic acid, H_2S, and soluble sulfides precipitate from neutral, slightly acid, or alkaline solutions of lead salts, lead sulfide, PbS, brownish black; insoluble in dilute acids, alkali hydroxides, carbonates or sulfides. Freshly precipitated metallic sulfides such as CdS, MnS, FeS, CoS and NiS will also precipitate PbS. Hydrosulfic acid and the soluble sulfides transpose all freshly precipitated lead salts to lead sulfide.[7] Ammonium

[1] Gupta, *J. Ch. Soc.*, (Proc.), **29**, 361–2 (1913).

[2] Reihlen and Kummer, *Ann.*, **469**, 30–44 (1929), state that $K_3Fe(CN)_6$ reacts with $Pb(NO_3)_2$ to give $FePb_2(CN)_6 \cdot NO_3 \cdot 5\frac{1}{2}H_2O$.

[3] Strömholm, *loc. cit.*

[4] Le Blanc and Noyes, *Z. physik. Ch.*, **6**, 385 (1890).

[5] Amat, *Compt. rend.*, **110**, 901 (1890).

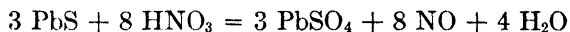
[6] Fairhill, *J. Am. Ch. Soc.*, **46**, 1593 (1924).

[7] It is shown from a consideration of the general theory of chemical reactions that, in the absence of disturbing factors, the least soluble compound is the first to precipitate

thioacetate precipitates at first lead sulfochloride, reddish; upon boiling this changes to black PbS. Moderately dilute HNO_3 (2–2.5 *N*) dissolves lead sulfide with separation of sulfur:

$$3\ PbS + 8\ HNO_3 = 3\ Pb(NO_3)_2 + 3\ S + 2\ NO + 4\ H_2O$$

Some of the sulfur, especially if the acid be concentrated, is oxidized to sulfate which will precipitate a portion of the lead unless the HNO_3 is present in sufficient amount to hold the $PbSO_4$ in solution.[1]

$$3\ PbS + 8\ HNO_3 = 3\ PbSO_4 + 8\ NO + 4\ H_2O$$

If a solution is too strongly acid, especially with HCl (1.4 *N* and higher), either no precipitation of PbS takes place, or a red double salt, PbCl·S·PbCl, is formed,[2] (the precipitation is incomplete).[3] Neutral salts, especially chlorides, lower very distinctly the concentration of HCl necessary to prevent precipitation of PbS from dilute lead chloride solution.[4] Sodium sulfide will detect one part of lead in 2,840,000 parts of water,[5] a test which is much more delicate than that involving the formation of the sulfate.

Ferric chloride oxidizes lead sulfide, forming $PbCl_2$, $FeCl_2$ and sulfur. The reaction takes place in the cold, more rapidly when warm. Iodine reacts readily with lead sulfide even in a dry mixture. With dry $KHSO_4$ hydrogen sulfide is evolved.

Lead thiosulfate, PbS_2O_3, white, is precipitated by adding $Na_2S_2O_3$ to the solution of a lead salt. The precipitate is readily soluble in excess of reagent, forming the complex $PbS_2O_3 \cdot 2Na_2S_2O_3$. On boiling, especially in the presence of NH_4Cl, the lead is quantitatively precipitated as the sulfide.[6]

Sodium sulfite precipitates lead sulfite, $PbSO_3$, white, less soluble in water than the sulfate;[7] slightly soluble in H_2SO_3; decomposed by sulfuric, nitric, hydrochloric and hydrosulfic acids and by alkali sulfides; not decomposed by cold phosphoric or acetic acid.

Sulfuric acid and solutions of sulfates precipitate from neutral or acid solution, lead sulfate, $PbSO_4$, white, not readily changed or permanently dissolved by acids, except H_2S, slightly soluble in strong acids (5, *c*); soluble in the fixed alkalis, moderately soluble in concentrated solutions

in a given case. In the instance under consideration PbS is the least soluble of the common lead salts.

[1] The oxidation of sulfur always occurs when HNO_3 acts upon sulfides, and in degree dependent upon the strength of acid, temperature, and duration of contact.

[2] Parmentier, *Compt. rend.*, **114**, 299 (1892).

[3] Dede and Bonin, *Ber.*, **55B**, 2327 (1922).

[4] Dede and Becker, *Z. anorg. allgem. Ch.*, **152**, 185 (1926).

[5] Eegriwe, *Z. anal. Ch.*, **53**, 420 (1914).

[6] Faktor, *Z. anal. Ch.*, **39**, 352 (1900).

[7] Ivanov, *Giorn. farm. ch.*, **64**, 259 (1915); *C. A.* **10**, 1826.

of ammonium salts, especially the acetate, tartrate, and citrate;[1] soluble in warm $Na_2S_2O_3$ solution, which decomposes on stronger heating with precipitation of PbS, insoluble in thiosulfate; (distinction and separation from $BaSO_4$, which does not dissolve in thiosulfates or ammonium acetate).[2]

The test for lead using SO_4^{--} is about twenty-five times less delicate than that employing H_2S or Na_2SO_3,[3] yet lead is quantitatively separated as the sulfate by precipitation with H_2SO_4 in moderate excess. When heated with K_2CrO_4 transposition of lead sulfate takes place and yellow $PbCrO_4$ is formed (6, *h*). Excess of KI also transposes lead sulfate (6, *f*), a distinction from barium. Repeated washing of lead sulfate with a solution of NaCl completely transposes the lead to chloride.

f. Hydrofluoric acid and soluble fluorides precipitate, from solutions of lead salts, lead fluoride, PbF_2, white, sparingly soluble in water or HNO_3; practically insoluble in HF; more soluble in HCl; slowly soluble in NaOH.[4] Its solubility in alkali halides increases with the atomic weight of the halide. The properties of lead fluoride are closer to those of lead oxide than to those of the other halides.[5] It is decomposed by H_2SO_4, forms the oxy-fluoride in presence of NH_4OH, and is practically unaffected by chlorine or iodine.

Hydrochloric acid and soluble chlorides precipitate, from solutions not too dilute, lead chloride, $PbCl_2$, white. The solubility of the precipitate (5, *c*) is such that the filtrate, obtained in the cold, gives good tests for Pb^{++} with H_2S, H_2SO_4, chromates, etc.[6] Hence, small amounts of lead will escape detection in Group I,[7] while its removal may be completely effected in Group II.

Hydrobromic acid and soluble bromides precipitate lead bromide, $PbBr_2$, white, somewhat less soluble in cold water than the chloride (5, *c*); soluble in excess of concentrated KBr as a complex salt which is decomposed with precipitation of $PbBr_2$ by dilution with water; soluble in NaOH.

Hydriodic acid and soluble iodides precipitate lead iodide, much less soluble in water than the chloride or bromide (5, *c*); soluble in hot, moderately concentrated HNO_3 and in solutions of the fixed alkalis, forming complex iodides as $NaPbI_3$ or Na_2PbI_4.[8] These salts are decomposed by

[1] Fox, *J. Ch. Soc.*. (Trans.), **95**, 878 (1909); Blomberg, *Ch. Weekblad*, **11**, 1030 (1914); Marden, *J. Am. Ch. Soc.*, **38**, 310 (1916).

[2] See, however, Marden, *loc. cit.*

[3] See references under lead sulfite.

[4] Brunner, *Helv. Ch. Acta*, **3**, 824 (1920).

[5] Sandonnini, *Atti. accad. Lincei*, [5] **23**, i, 959 (1914); *Chem. Zentr.*, **85**, II, 818.

[6] Failure of such tests may be due to excess Cl^- or high H^+. See especially 6, *e*.

[7] For solubility of lead chloride in HCl see Mellor, VII, 714.
Craig, *Metal Ind.*, (New York), **20**, 338 (1922).
Kendall and Sloan, *loc. cit.*

[8] Herty, *Am. Ch. J.*, **14**, 107 (1892); **15**, 97 (1893); **18**, 290 (1896).

addition of water with precipitation of the lead iodide. PbI_2 is not precipitated in the presence of excess acetate (not acetic acid);[1] alkali citrates also prevent precipitation to some extent. Lead iodide is readily soluble in $Na_2S_2O_3$. Freshly precipitated PbO_2 gives free iodine when treated with KI.

When detecting lead as the iodide in solutions of the chloride by precipitation with KI and recrystallization of the yellow precipitate from hot water, care must be exercised that the reagent be not added in excess sufficient to form the soluble double iodide.

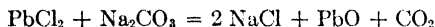
Iodic acid or soluble iodates precipitate, from solutions of lead salts, white lead iodate, $Pb(IO_3)_2$, soluble in water to the extent of 0.018 g./l. at 17°;[2] solubility increased by KNO_3 or $Pb(NO_3)_2$ (over 0.05 N);[3] insoluble in $HC_2H_3O_2$; difficultly soluble in HNO_3.

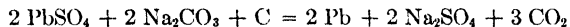
g. Arsenites precipitate from solutions of lead salts, bulky, white, lead orthoarsenite, $Pb_3(AsO_3)_2 \cdot xH_2O$, difficultly soluble in water, readily soluble in dilute acids and fixed alkali hydroxides.[4] Soluble arsenates precipitate white lead arsenate from neutral or slightly alkaline solutions of lead salts; soluble in the fixed alkali hydroxides and HNO_3; insoluble in $HC_2H_3O_2$. The composition of the precipitate depends upon conditions; it appears to be a mixture of $Pb_3(AsO_4)_2$ and $PbHAsO_4$.[5]

Hot Na_2SnO_2 gives, with lead salts or lead hydroxide, a black precipitate of metallic lead.

h. Chromic acid and soluble chromates (or dichromates) precipitate lead chromate, $PbCrO_4$, yellow; soluble in fixed alkali hydroxides (distinction from bismuth); insoluble in excess of chromic acid (distinction from barium); insoluble in NH_4OH (distinction from silver); soluble in approximately 3 N HNO_3; decomposed by moderately concentrated HCl; insoluble in $HC_2H_3O_2$ (distinction from bismuth).

7. Ignition. — Lead salts, when fused with Na_2CO_3 are converted into lead oxide, PbO:

$$PbCl_2 + Na_2CO_3 = 2\ NaCl + PbO + CO_2$$

If charcoal or some organic compound as sugar, tartrates, etc., be present, metallic lead is formed:

$$2\ PbSO_4 + 2\ Na_2CO_3 + C = 2\ Pb + 2\ Na_2SO_4 + 3\ CO_2$$

With excess of charcoal the acid radical may also be reduced:

$$2\ PbSO_4 + 2\ Na_2CO_3 + 5\ C = 2\ Pb + 2\ Na_2S + 7\ CO_2$$

[1] An example of common-ion effect. Lead acetate is slightly ionized. In the presence of excess acetate the ionization is repressed to such an extent that insufficient PbI_2 is formed to more than saturate the solution. Non-precipitation has also been explained in this case on the basis of formation of a complex lead acetate ion.

[2] Kohlrausch, *Z. physik. Ch.*, **64**, 151, 168 (1908).

[3] Harkins and Pearce, *J. Am. Ch. Soc.*, **38**, 2705 (1916).

[4] Stavenhagen, *J. prakt. Ch.*, [2] **51**, 33 (1895).

[5] McDonnell and Smith, *J. Am. Ch. Soc.*, **39**, 937 (1917); Tartar and Robinson, *Ibid.*, **36**, 1843 (1914); Curry and Smith, *Ibid.*, **37**, 1685 (1915); Smith, *Ibid.*, **38**, 2014 (1916).

8. Detection.[1] — Lead is precipitated (incompletely) from its solutions by HCl as $PbCl_2$, separated from AgCl and Hg_2Cl_2 by hot water and confirmed by means of H_2SO_4, $K_2Cr_2O_7$ and KI. Lead is separated from arsenic, antimony and tin, in Group II by taking advantage of the insolubility of PbS in $(NH_4)_2S_x$ or $Na_2S + NaOH$; from HgS by HNO_3; from Bi, Cu and Cd by precipitation of the sulfate with H_2SO_4. Insoluble compounds may be transposed by an alkali sulfide, being then treated as lead in the second group; or they may be fused with Na_2CO_3 and the residue, obtained after extraction with water, dissolved in acid and tested for lead.[2]

Among the various organic reagents indicated for the detection of lead are the following: (a) Diphenylthiocarbizide, a 5% alcoholic solution, gives a characteristic, flocculent, orange precipitate with Pb^{++};[3] (b) in a hot, slightly alkaline solution, 8-hydroxyquinoline gives a quantitative precipitation of lead;[4] (c) benzidine acetate[5] and (d) tetramethyldiaminodiphenylmethane[6] are said to give characteristic reactions with lead.

9. Determination.[7] — Lead may be separated (1) as the sulfate from all metals except Ba, Sr and Ca; (2) electrolytically as the dioxide[8] from all but Ag, As, Sb, Sn, Cr and Mn; (3) as the sulfide from ions of Groups III, IV and V; (4) as the molybdate from Cu, Zn, Ni, Co and Mn.[9] *Gravimetrically* lead may be determined as the sulfate, molybdate or dioxide. (a) The sulfate method involves evaporation of the solution with H_2SO_4 to fumes of SO_3, dilution, filtration and washing the precipitate with dilute H_2SO_4. In this way a separation[10] is effected from practically all of the common metals. The purified[11] $PbSO_4$ is dried at 600–700°, cooled and weighed. (b) While the molybdate method is very accurate it requires careful manipulation to avoid a colloidal precipitate difficult to filter. The hot, slightly acid (HCl or HNO_3) solution is first treated with an excess of ammonium molybdate then $NH_4C_2H_3O_2$ is added to reduce the acidity and thus insure complete precipitation. After filtration and washing the precipitate is ignited and weighed as $PbMoO_4$. The method offers a means of separating lead from Cu, Mn, Zn, Co, and Ni. (c) Lead may be deposited electrolytically as PbO_2 on a platinum gauze anode from a nitric acid solution. The method is rapid, accurate and satisfactory in the presence of many metals.

Volumetrically lead may be determined as the chromate or molybdate. (a) In the chromate method the $PbCrO_4$ may be dissolved in HCl, KI added and the liberated iodine titrated with $Na_2S_2O_3$. (b) In the molybdate method the solution of $Pb(C_2H_3O_2)_2$ is titrated with ammonium molybdate, the endpoint being determined by means of tannic acid as an external indicator.

[1] Cf. Mitchell, II, 21–2 for recent advances in micro tests.
[2] For the delicacy of some tests for lead see Eegriwe, *Z. anal. Ch.*, **53**, 420–6 (1914).
[3] Parri, *Giorn. farm. ch.*, **73**, 207–14 (1924).
[4] Marsson and Haase, *Ch. Ztg.*, **52**, 993 (1928).
[5] Feigl and Neuber, *Z. anal. Ch.*, **62**, 371 (1923).
[6] Carney, *J. Am. Ch. Soc.*, **34**, 32 (1912).
[7] For difficulties in the separation and estimation of small amounts of lead see Breteau and Fleury, *J. pharm. ch.*, **10**, 147, 265 (1914).
[8] Especially important when dealing with the combination Cu-Pb.
[9] Cf. Mitchell, II, 24–30.
[10] See, however, Marden, *J. Am. Ch. Soc.*, **38**, 310 (1916), for incompleteness of separation from alkaline earth sulfates.
[11] By means of $NH_4C_2H_3O_2$.

10. Oxidation and Reduction. — Metallic lead precipitates the free metal from solutions of Hg, Ag, Au, Pt, Bi and Cu. Bivalent lead is oxidized to Pb^{+4} as stated above (4), also electrolytically in the separation from copper. In the presence of dilute H_2SO_4, Pb^{+4} is reduced to Pb° by nascent hydrogen, and by all metals capable of producing nascent hydrogen (such as Al, Zn, Sn, Mg and Fe), and to Pb^{++} by Hg_2^{++}, Sn^{++}, Sb^{+3}, As^{+3}, AsH_3, Cu_2^{++}, Fe^{++}, Cr^{+3}, Mn^{++}, Mn^{7-n}; also by $H_2C_2O_4$, HNO_2, H_3PO_2, H_3PO_3, P°, SO_2, H_2S, HCl, HBr, HI, HCN, HCNS, $H_4Fe(CN)_6$, glycerine, tartaric acid, sugar, and very many other organic compounds. In many cases the reduction to Pb^{++} or to Pb° takes place in the presence of NaOH. The freshly precipitated peroxide oxidizes ammonia to nitrite and nitrate in the course of a few hours.

Solutions of Pb^{++} yield precipitates of Pb° when treated with Zn°, Mg°, Al°, Cd°, etc.

§58. Mercury (Planet *Mercury*) (Hydrargyrum) Hg = 200.61. Valence 1 and 2. Atomic No. 80. Discovery, at least as early as 300 B.C.

1. Physical Properties. — Density, liquid, 13.595, 0°/4°,[1] *solid*, 14.19 at −38.9°;[2] *melting point*, −38.87° ± 0.01°;[3] boiling point, 356.95°.[4] Mercury is the only metal that is a liquid at ordinary temperatures. (Gallium melts at 29.75°.) It has a brilliant, silvery luster with a slightly bluish tinge; the finely divided metal appears as a dark gray powder. (This condition is readily obtained by shaking with sugar, grease, chalk, ether, etc.) It is slightly volatile even at −13°; is not oxidized by air or oxygen at ordinary temperatures; is slowly converted to the oxide by heating near the boiling point. The solid metal is very ductile and easily cut with a knife. It forms a convex surface when in a glass container. It is a fair conductor of heat and electricity and has a regular coefficient of expansion. It dissolves many metals forming amalgams (not Fe or Pt).

2. Occurrence. — Cinnabar, HgS, red to brownish red, is the chief mercury mineral. Occasionally the free metal is found as a very minor component of the ore. In 1927 the world's production of mercury was approximately 150,000 flasks (76 lbs. each) of which Spain furnished 47%; Italy, 43%; and the United States (chiefly California), 7.5%. All of Spain's supply comes from one mine — the Almaden — which is one of the most famous in the world. It is said to have been continuously worked for over 2500 years.[5]

3. Preparation. — The ore is roasted with a regulated supply of air ($HgS + O_2 = Hg + SO_2$) and the vapor passed through a condensing system where the mercury is collected. After filtration through cloth or leather to free it from dirt the metal is bottled in iron flasks. With ores running low in mercury content, e.g., some U. S. ores contain 0.4% or less (European ores run about 7%), a preliminary concentration may be employed.

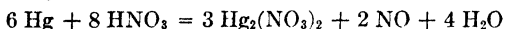
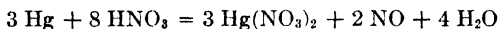
4. Oxides. — Mercury forms three oxides, Hg_2O, HgO and HgO_2. Mercurous oxide, Hg_2O, is a black powder formed by the action of fixed alkalis on mercurous salts. When heated it is converted into Hg° and HgO or Hg° and O_2, depending upon conditions. Exposure to light also results in decomposition. Mercuric oxide, HgO, is made (a) by

[1] Scheel and Blankenstein, *Z. physik*, **31**, 202 (1925).
[2] I. C. T.
[3] Henning and Heuse, *Z. physik*, **23**, 95–104 (1924).
[4] Smith and Menzies, *J. Am. Ch. Soc.*, **32**, 1446 (1910).
[5] *Mineral Ind.*, 1927, 514.

keeping mercury at its boiling point for a month or more in contact with air; (b) on a large scale by heating $Hg_2(NO_3)_2$ or a mixture of $Hg(NO_3)_2$ and Hg until no further red fumes of NO_2 are given off; (c) by treating a mercuric salt with fixed alkali. The first two methods yield a bright red product, the third gives a yellow oxide. It is claimed that the color is due to the state of division, yellow HgO being the finer. A similar explanation is offered for its greater reactivity. On heating, HgO changes to vermillion, then black; when cooled it regains its original color. At higher temperatures it is decomposed into Hg and O_2. Mercuric peroxide, HgO_2, reddish brown, has been prepared by treating $Hg(NO_3)_2$ with an excess of perhydrol at 0°.[1] It is fairly stable in air and slowly decomposed by water. Apparently the existence of hydroxides of mercury is still an unsettled question.

5. Solubilities. — *a. Metal.* — Mercury is unaffected by treatment with alkalis. HNO_3 is the most effective solvent if a small amount of HNO_2 is present. Ferric iron has a marked retarding effect; manganous and sodium ions accelerate solution.[2] Solution in dilute acid, hot or cold, is readily effected; if strong acid is used much heat is evolved and the rate may reach explosive violence. At ordinary temperatures if the HNO_3 is in excess $Hg(NO_3)_2$ is formed; if the Hg is in excess $Hg_2(NO_3)_2$ is obtained:

$$3\,Hg + 8\,HNO_3 = 3\,Hg(NO_3)_2 + 2\,NO + 4\,H_2O$$

$$6\,Hg + 8\,HNO_3 = 3\,Hg_2(NO_3)_2 + 2\,NO + 4\,H_2O$$

Both $Hg_2(NO_3)_2$ and $Hg(NO_3)_2$ require an excess of free acid to prevent hydrolysis and hold them in solution. In case of the $Hg_2(NO_3)_2$ this excess acid oxidizes the mercurous salt to mercuric; this precipitates as the basic nitrate as the acid is used up, or remains in solution as $Hg(NO_3)_2$ depending upon the amount of free acid. A solution of $Hg_2(NO_3)_2$ may be kept free from $Hg(NO_3)_2$ for a short time by placing some metallic Hg in the bottle. After standing some weeks a basic mercurous nitrate crystallizes out, which may be dissolved by addition of HNO_3. Sulfur attacks mercury forming HgS.[3] Dry H_2S at ordinary temperatures does not react with Hg; if oxygen is present the sulfide is formed, water vapor retards the reaction.[4] $Na_2S_2O_3$ reacts with Hg forming HgS.[5] Hg is not attacked by cold aqueous solutions of SO_2 either alone or in the presence of HCl or H_2SO_4.[6] Dilute H_2SO_4 or the concentrated acid at 25° has no effect upon Hg.[7] Hot concentrated H_2SO_4 forms Hg_2SO_4 if the Hg is in excess, $HgSO_4$ if the acid is in excess.[8] ($2\,Hg + 2\,H_2SO_4 = Hg_2SO_4 + SO_2 + 2\,H_2O$; $Hg + 2\,H_2SO_4 = HgSO_4 + SO_2 + 2\,H_2O$.)

F, Cl, Br and I all attack Hg forming mercurous salts if Hg is in excess, mercuric salts if the halogen is in excess. HF, either gaseous or an aqueous solution, does not attack Hg; the same is true of cold HCl; HBr reacts slowly in the cold, more rapidly when hot. HI reacts rapidly yielding Hg_2I_2 or HgI_2 (H_2HgI_4 if HI is in excess) depending upon conditions.

b. Oxides and Hydroxides. — Mercurous oxide, black, is insoluble in water.[9] HCl forms Hg_2Cl_2; H_2SO_4 forms Hg_2SO_4 which upon boiling with excess acid becomes $HgSO_4$; HNO_3 forms $Hg_2(NO_3)_2$ which is oxidized by excess acid to $Hg(NO_3)_2$; completely soluble in concentrated $HC_2H_3O_2$. Mercuric oxide, yellow, dissolves in water at 25°, to the extent of 0.05 g. per liter; the red form probably has the same solubility.[10] It is somewhat more soluble in solutions of the fixed alkalis than in water; soluble in

[1] Pellini, *Atti. accad. Lincei*, [5] **16**, II, 408 (1907); *Gazz. ch. ital.*, **38**, 71 (1908).

[2] Ray, *J. Ch. Soc.*, **99**, 1012 (1911).

[3] Schrotter, *J. Ch. Soc.*, **26**, 476 (1873).

[4] Berthelot, *Compt. rend.*, **125**, 746 (1897).

[5] Brunck, *Ann.*, **327**, 250 (1903).

[6] Berthelot, *Ann. ch. phys.*, [7] **14**, 198 (1898).

[7] Taboury, *Compt. rend.*, **190**, 1428–30 (1930); *C.A.* **24**, 4476, says that at about 20° H_2SO_4 reacts with Hg. to give SO_2.

[8] Baskerville and Miller, *J. Am. Ch. Soc.*, **19**, 874 (1897); **20**, 515 (1898).

[9] Immerwahr, *Z. Elektroch.*, **7**, 478, 482 (1901).
See also Allmand, *Ibid.*, **16**, 263 (1910).

[10] Schick, *Z. physik. Ch.*, **42**, 172 (1903).

acids except H_3PO_4 and H_3AsO_4, (sulfurous acid gives $Hg + H_2SO_4$; H_3PO_3 reacts similarly); soluble in solutions of alkali and alkaline earth chlorides due to the formation of slightly ionized $HgCl_2$; soluble in KI giving K_2HgI_4.

c. Salts. — Mercury forms two classes of salts — mercurous, univalent, and mercuric, bivalent. Most mercurous compounds are permanent in air, but are changed by powerful oxidizing agents to the higher valence. While the latter are somewhat more stable, they are changed by many reducing agents, first to mercurous compounds then to metallic mercury. Solutions of mercury salts are acid to litmus. Many of the salts are either insoluble in water, or require the presence of free acid to prevent hydrolysis which would result in the precipitation of a basic salt and leave an acid, supernatant liquid. The solubility data for mercurous halides in water at 25° are very discordant.[1] The data for mercuric halides in water at 25° are as follows:

$HgCl_2$	$HgBr_2$	HgI_2
67.6 g./l.[2]	6.135 g./l.[3]	0.059 g./l.[4]
		(0.2–0.4 mg./l. at 18°)[3]

Hg_2SO_4 is slightly soluble in water (0.39 g./l.),[5] but soon decomposes with precipitation of a basic salt; it is soluble in HNO_3 and dilute H_2SO_4. $Hg_2(C_2H_3O_2)_2$ dissolves to the extent of 1.067 g./l.[6] $Hg_2(NO_3)_2$ is soluble in water but the presence of free HNO_3 is necessary to prevent the precipitation of a basic salt. On standing $Hg_2(NO_3)_2$ gradually changes to $Hg(NO_3)_2$; this is prevented by the presence of Hg°, but if Hg° be present the excess HNO_3 is gradually used up and a precipitate of basic mercurous nitrate forms (see 5, *a*).

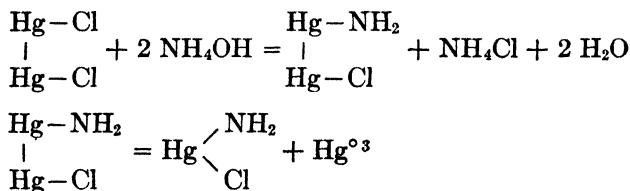
In aqueous solutions $HgCl_2$ associates to produce $(HgCl_2)_2$ which according to Linhart[7] is the only complex formed in H_2O at any temperature or concentration. $HgBr_2$ is decomposed by warm HNO_3 or H_2SO_4. HgI_2 is soluble in $Na_2S_2O_3$ and in many alkali and alkaline earth salts, forming double salts. Normal $HgSO_4$ reacts with water, a precipitate of the basic sulfate being formed; this is prevented if free H_2SO_4 is present. Normal mercuric nitrate is deliquescent and soluble in a small amount of water; dilution results in the precipitation of a basic salt readily soluble in HNO_3.

[1] Kohlrausch, *Z. physik. Ch.*, **64**, 150 (1908); Rolla, *Atti. accad. Lincei*, [5] **22**, II, 104 (1913); Spencer, *Z. physik. Ch.*, **80**, 701 (1912); Brodsky and Schershewer, *Z. Elektroch.*, **32**, 1–4 (1926).
[2] Moles and Marquina, *Ann. soc. españ. fís. quím.*, **22**, 551–4 (1924); *C.A.* **19**, 1218. Herz and Paul, *Z. anorg. allgem Ch.*, **82**, 431 (1913).
[3] Morse, *Z. physik. Ch.*, **41**, 709–34 (1902).
[4] Kohlrausch, *Z. physik. Ch.*, **64**, 150 (1908).
[5] Wilsmore, *Z. physik. Ch.*, **35**, 305 (1900).
[6] Teltscher, Dissert. München, **1912**, 61.
[7] Linhart, *J. Am. Ch. Soc.*, **37**, 258–74 (1915); cf. 6, *f*, Bourion and Rouyer.

Mercuric cyanide is soluble to the extent of 100 g./l.[1] The acetate is readily soluble, the chromate is decomposed, and the sulfide, iodide, basic carbonate, oxalate, phosphate, arsenite, arsenate and ferrocyanide are insoluble in water.

6. Reactions. — *a.* Fixed alkali hydroxides precipitate, from solutions of mercurous salts, mercurous oxide, Hg_2O, black, insoluble in excess alkali, readily transposed by acids; from mercuric salts NaOH (or KOH) precipitates (a) reddish-brown basic salts when added in less than equivalent amounts, and (b) the yellow mercuric oxide, HgO, when added in excess. If the solution of mercuric salt be strongly acid incomplete precipitation of HgO may be obtained owing to the solubility of the oxide in the alkali salt formed or possibly to the formation of a complex salt, e.g., Na_2HgCl_4. NH_4OH and $(NH_4)_2CO_3$ precipitate from solutions of mercurous salts mixtures of mercury and mercuric amino compounds. Insoluble mercurous salts are similarly transposed by NH_4OH:[2]

$$\begin{matrix} Hg-Cl \\ | \\ Hg-Cl \end{matrix} + 2\,NH_4OH = \begin{matrix} Hg-NH_2 \\ | \\ Hg-Cl \end{matrix} + NH_4Cl + 2\,H_2O$$

$$\begin{matrix} Hg-NH_2 \\ | \\ Hg-Cl \end{matrix} = Hg\begin{matrix} \diagup NH_2 \\ \diagdown Cl \end{matrix} + Hg^{\circ}$$ [3]

Mercuri-ammonium compounds have been divided into three groups:[4]

(1) Additive compounds;
(2) Ammonolyzed compounds in which NH_2, NH or N takes the place of the acid radical in a mercuric salt;
(3) Both hydrolyzed and ammonolyzed compounds.

If $HgCl_2$ is slowly added to a hot mixture of NH_4OH and NH_4Cl the so-called fusible white precipitate, $HgCl_2 \cdot 2NH_3$, is formed, an example of (1) above. On the other hand if NH_4OH is added to $HgCl_2$ infusible white precipitate, NH_2HgCl, is obtained, an example of (2) above. The addition of NH_3 to HgI_2 or, more readily, the reaction between NH_3 and Nessler's reagent (alkaline K_2HgI_4) produces a reddish-brown precipitate, the so-called iodide of Millon's base, example of (3) above for which

[1] Hofmann and Wagner, *Z. Elektroch.*, **15**, 444 (1909).

[2] While mercurous ammonia compounds have been postulated as probable intermediate products none of them appear to have been isolated and identified.

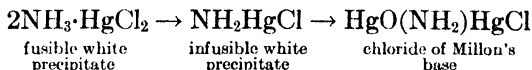
[3] Feigl and Sucharipa, *Z. anal. Ch.*, **67**, 134 (1925). Cf. Druce, *Chem. News*, **123**, 153 (1921); **126**, 225 (1923). Saha and Choudhuri, *Z. anorg. allgem. Ch.*, (*Chloride*) **67**, 357 (1910); (*Nitrate*) **71**, 309 (1911); (*Bromide and iodide*) **77**, 41 (1912); (*Carbonate and sulfate*) **86**, 239 (1914).

[4] Holmes, *J. Ch. Soc.* (Trans.), **113**, 74 (1918).

various formulas have been given. Two of them are:

$$O\begin{array}{l}\diagup Hg \diagdown \\ \diagdown Hg \diagup\end{array} N \begin{array}{l} \diagup H \\ - H \\ \diagdown I \end{array} \qquad \begin{array}{l} H \\ | \quad \diagup I \\ N - Hg - O - H \end{array}$$

The relationship between these three types of compounds has been indicated thus:[1]

$$\underset{\text{fusible white precipitate}}{2NH_3 \cdot HgCl_2} \rightarrow \underset{\text{infusible white precipitate}}{NH_2HgCl} \rightarrow \underset{\text{chloride of Millon's base}}{HgO(NH_2)HgCl}$$

Alkali carbonates precipitate from solutions of $Hg_2(NO_3)_2$ yellow, impure mercurous carbonate, Hg_2CO_3, which readily decomposes into Hg and HgO when heated and darkens on exposure to light. Bicarbonates of the alkalis and carbonates of the alkaline earth metals also precipitate Hg_2CO_3. Mercuric carbonate, $HgCO_3$, reddish brown, is obtained upon passing CO_2 into an alkaline solution of $HgCl_2$.[2] Upon adding $Hg(NO_3)_2$ to an alkali carbonate the brownish precipitate obtained is $4HgO \cdot CO_2$ (also written $Hg_4O_3CO_3$); if a bicarbonate is used $3HgO \cdot CO_2$ (also written $Hg_3O_2CO_3$) results. On the other hand if the carbonate be added to mercuric chloride a basic chloride is precipitated, the exact composition apparently depends upon conditions such as temperature, concentration, etc. Alkaline earth carbonates precipitate a basic salt from solutions of $Hg(NO_3)_2$ or $HgSO_4$ but not from $HgCl_2$.

b. Oxalic acid and soluble oxalates precipitate from mercurous salts white, mercurous oxalate, $Hg_2C_2O_4 \cdot H_2O$, insoluble in dilute HNO_3 or H_2SO_4, becomes dirty yellow after long contact with cold water, darkens in hot water, slightly more soluble in $H_2C_2O_4$ than in water. Mercuric oxalate, HgC_2O_4, white, explosive, readily soluble in HCl, insoluble in cold water or $H_2C_2O_4$, difficultly soluble in HNO_3, is precipitated from solutions of $Hg(NO_3)_2$ or $HgSO_4$ but not from $HgCl_2$.

Mercurous acetate, $Hg_2(C_2H_3O_2)_2$, is less soluble in water than mercuric acetate, $Hg(C_2H_3O_2)_2$; both darken on exposure to light.

Hydrocyanic acid and soluble cyanides decompose mercurous salts into metallic mercury and $Hg(CN)_2$;[3] mercuric salts form the readily soluble, but slightly ionized, mercuric cyanide $Hg(CN)_2$.[4] Excess cyanide forms

[1] Weitz, *Ann.*, **410**, 117 (1915). For further discussion of the reactions of mercury with NH_4OH see in addition to the references already given:

Gaudechon, *Ann. ch. phys.*, [8] **22**, 145–247 (1911); Franklin, *Am. Ch. J.*, **47**, 361–97 (1912); Ray and Banerji, *J. Indian Ch. Soc.*, **5**, 715–9 (1928), *C.A.*, **23**, 1834; François, *Ann. ch.*, [10] **11**, 22–44 (1929), *C.A.* **24**, 1051.

[2] Raikow, *Chem. Ztg.*, **31**, 55, 87 (1907).

[3] Abel, *Z. anorg. allgem. Ch.*, **26**, 379 (1901).

[4] Hofmann, *Ch. Ztg.*, **32**, 78 (1908); Gupta, *J. Ch. Soc.*, **117**, 67–73 (1920) (Action $Hg(CN)_2$ on metallic salts); Pertusi, *Ch. Ztg.*, **38**, 1203–4 (1914) (Reactions of $Hg(CN)_2$); Esteve, *Ibid.*, **35**, 1152 (1911) (Action of HCN on Hg halides); Bourion and Rouyer, *Compt. rend.*, **178**, 1171–4 (1924).

soluble complexes with alkali chlorides, e.g., $KHg(CN)_2Cl$, $K_2Hg(CN)_4$, etc. $Hg(CN)_2$ is the only cyanide of the heavy metals that is soluble in water. No precipitate is obtained when alkali hydroxides or carbonates are added to $Hg(CN)_2$.

Soluble ferrocyanides give with solutions of mercurous salts a gelatinous, pale yellow precipitate that in a short time becomes bluish green; with mercuric salts a gelatinous white precipitate that slowly becomes blue upon standing. Formulas for these precipitates are unknown. Soluble ferricyanides give with mercurous salts yellowish to green mercurous ferricyanide, $Hg_3Fe(CN)_6$;[1] with mercuric chloride no precipitate; with mercuric nitrate a reddish-brown, gelatinous precipitate of $Hg_3[Fe(CN)_6]_2$[2] turning yellow upon standing. Soluble thiocyanates give a gray precipitate with mercurous salts; with mercuric salts of moderate concentration (not $HgCl_2$) a white precipitate of mercuric thiocyanate, $Hg(CNS)_2$, soluble in excess of reagent, and in hot water.

c. Nitric acid does not act as a precipitant of mercury salts; they are more soluble in concentrated HNO_3 than in water or the dilute acid. Nitric acid dissolves all insoluble salts of mercury except HgS, which, however, may be converted to the more soluble complex $2HgS{\cdot}Hg(NO_3)_2$, white, by boiling with concentrated acid. All mercurous salts are oxidized to mercuric salts by excess of HNO_3. (This explains the solubility of Hg_2Cl_2 in boiling HNO_3.) Hydroxylamine and hydrazine reduce mercuric salts, in presence of an alkali, to Hg°. In presence of strong acids the reduction is incomplete.[3]

d. Hypophosphorous and phosphorous acids reduce mercuric salts to mercurous and Hg°; in case of the latter reagent Hg° is obtained only at higher temperatures.[4] Phosphoric acid and alkali phosphates, e.g., Na_2HPO_4 precipitate from mercurous salts, white Hg_3PO_4 if the reagent be in excess, but if $Hg_2(NO_3)_2$ be in excess, $Hg_2O{\cdot}2HgNO_3{\cdot}5Hg_3PO_4{\cdot}H_2O$,[5] somewhat yellowish. Hg_3PO_4 is soluble in HNO_3, insoluble in H_3PO_4. From solutions of $Hg(NO_3)_2$ containing excess acid, white $Hg_3(PO_4)_2$ is precipitated by Na_2HPO_4; somewhat soluble in hot water; soluble in HCl and NH_4Cl, less readily in HNO_3; insoluble in H_3PO_4. Phosphoric acid does not produce a precipitate from solutions of $HgCl_2$, nor does Na_2HPO_4 give the normal salt, but on standing for some time a portion of the mercury separates as a dark brown precipitate.[6] $Na_4P_2O_7$ gives with $Hg_2(NO_3)_2$, $Hg_4P_2O_7{\cdot}H_2O$, white, darkening on heating, soluble

[1] Fernekes, *J. Am. Ch. Soc.*, **28**, 604 (1906).
[2] *Idem.*
[3] DeMetz, *Ch. Weekblad*, **21**, 91 (1924).
[4] Garner, *et al.*, *Am. Ch. J.*, **46**, 361 (1911); Linhart, *Am. J. Sci.*, **35**, 353–68 (1913).
[5] Haack, *Ann.*, **262**, 192 (1891).
[6] Haack, *J. Ch. Soc.*, **60**, 400 (1891); **62**. 530 (1892).

in excess reagent and HNO_3; with $Hg(NO_3)_2$ a white precipitate of $Hg_2P_2O_7$ later turning yellow is obtained, soluble in acids and aqueous NaCl.

e. Among all the metals Hg has the greatest affinity for sulfur. (There may be one exception, Pd.) Hydrosulfic acid and soluble sulfides precipitate from mercurous salts at room temperature mercuric sulfide, HgS, black, and metallic mercury. Mercurous sulfide is said to be stable only below 0°. Solutions of mercuric salts[1] give, with sulfides, first a white precipitate ($HgCl_2 \cdot 2HgS$) rapidly changing on addition of more reagent to yellow, red, brown and finally black. This succession of colors is characteristic of mercury. While the black modification is the one finally obtained in analytical work it is claimed that this is a meta-stable form, vermillion (cinnabar) being the stable. (To support this statement it is readily shown that the black is the more reactive of the two.) The black form may be converted into the red by grinding in a mortar or by sublimation. To account for the succession of colors it is said that the intermediates are complexes in which the ratio of $HgCl_2$ to HgS varies, the proportion of HgS being greater the darker the precipitate.[2] Mercuric sulfide is insoluble in dilute HNO_3 (see 6, *c*); distinctly soluble in concentrated HCl with liberation of H_2S; soluble in aqua regia; soluble in HCl + $KClO_3$; very slightly soluble in $(NH_4)_2S$ or the polysulfide,[3] less so in the latter than in the former; fairly soluble in fixed alkali hydroxides or sulfides, readily soluble in a mixture of the two, especially if the ratio of HgS : Na_2S = 1 : 2 (separation from Pb, Ag, Bi and Cu). Solubility is due to formation of Na_2HgS_2, ($Na_2S \cdot HgS$) Na_4HgS_3 ($2Na_2S \cdot HgS$) or Na_8HgS_5 ($4Na_2S \cdot HgS$); insoluble in cold NaHS; soluble in sodium thiocarbonate, Na_2CS_3, (separation from Pb, Bi and Cu) from which it is reprecipitated as HgS by HCl.

Ammonium thioacetate added to an acid solution of mercurous ions gives HgS and Hg°. If the reagent is added to a cold HCl solution of Hg^{++} a red precipitate is obtained which upon heating changes to black HgS. Mercurous nitrate forms with $Na_2S_2O_3$ a grayish-black precipitate, part of the mercury remaining in solution; mercurous chloride forms a soluble salt and metallic mercury. The product of the action of $Na_2S_2O_3$ on mercuric salts depends upon the ratio of the two salts in the solution, also upon the concentration:

[1] For action of H_2S on mercuric salts see Pélabon, *Bull. soc. ch.*, **37**, 854 (1925).

[2] Jolibois and Bouvier, *Compt. rend.*, **170**, 1497 (1920), claim that only black and white HgS exist as definite compounds.

[3] Christensen, *Ber. Pharm. Ges.*, **26**, 261 (1916); *J. Ch. Soc.*, **112**, II, 33 (1917).

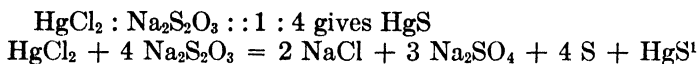
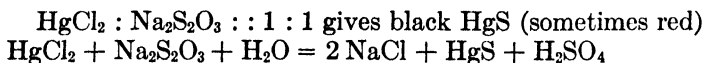
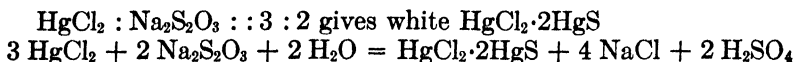
$HgCl_2 : Na_2S_2O_3 :: 3 : 2$ gives white $HgCl_2 \cdot 2HgS$

$$3\,HgCl_2 + 2\,Na_2S_2O_3 + 2\,H_2O = HgCl_2 \cdot 2HgS + 4\,NaCl + 2\,H_2SO_4$$

$HgCl_2 : Na_2S_2O_3 :: 1 : 1$ gives black HgS (sometimes red)

$$HgCl_2 + Na_2S_2O_3 + H_2O = 2\,NaCl + HgS + H_2SO_4$$

$HgCl_2 : Na_2S_2O_3 :: 1 : 4$ gives HgS

$$HgCl_2 + 4\,Na_2S_2O_3 = 2\,NaCl + 3\,Na_2SO_4 + 4\,S + HgS$$ [1]

Sulfurous acid and soluble sulfites form in mercurous solutions a gray black precipitate, $Hg_4(SO_3)_2 \cdot H_2O$, which upon standing at room temperature slowly decomposes into Hg_2SO_4, Hg° and SO_2; unstable in water; decomposing rapidly in warm water to $Hg^\circ + H_2SO_4$. $Hg(NO_3)_2$ gives, with sulfites, a voluminous white precipitate containing mercurous mercury; $HgCl_2$ gives no precipitate in the cold but is reduced by boiling with H_2SO_3 to Hg_2Cl_2 and then Hg°.

Sulfuric acid and soluble sulfates precipitate from sufficiently concentrated mercurous solutions, mercurous sulfate, Hg_2SO_4, white, sparingly soluble in cold water,[2] decomposed by boiling water into dirty yellow HgO and Hg°;[3] darkened by light; soluble in dilute HNO_3; more soluble in dilute H_2SO_4 than in H_2O; in saturated $CdSO_4$ solution about five times more soluble than in water.[4] Mercuric salts are not precipitated by H_2SO_4 or sulfates.

f. Mercurous and mercuric fluoride are both soluble in water.

Hydrochloric acid and soluble chlorides precipitate from mercurous solutions, white mercurous chloride, Hg_2Cl_2, "calomel"; soluble in concentrated HCl due to the formation of complexes. Boiling HNO_3 slowly dissolves Hg_2Cl_2 due to oxidation to Hg^{++}: $3\,Hg_2Cl_2 + 8\,HNO_3 = 3\,HgCl_2 + 3\,Hg(NO_3)_2 + 2\,NO + 4\,H_2O$. Chlorine or aqua regia dissolve Hg_2Cl_2 forming $HgCl_2$; soluble in $Hg(NO_3)_2$ due to the formation of slightly ionized $HgCl_2$; bromides and iodides both quantitatively displace the chloride from Hg_2Cl_2; sulfides give Hg° and HgS; soluble in $(NH_4)_2SO_4$; NH_4OH gives black $NH_2HgCl + Hg^\circ$ (see 6, *a*); soluble cyanides decompose Hg_2Cl_2 giving as one of the major products Hg°.[5] The precipitation of mercurous salts by HCl gives a sharp separation from mercuric salts since the latter form a soluble chloride (see 5, *c*).

Mercuric chloride is a slightly dissociated compound and in solution polymerizes, forming $(HgCl_2)_2$ and $(HgCl_2)_3$.[6] It also forms complex

[1] For a detailed discussion see:
Allen, *et al.*, *Am. J. Sci.*, [4] **34**, 367 (1912); Feld, *Z. angew. Ch.*, **24**, 290, 1161 (1911).

[2] Barre, *Ann. ch. phys.*, [8] **24**, 203 (1911).

[3] Cox, *Z. anorg. allgem. Ch.*, **40**, 180 (1904).

[4] Hulett, *Phys. Rev.*, **25**, 16 (1907).

[5] Wollschläger, *Pharm. Ztg.*, **57**, 544 (1912).
Esteve, *Ch. Ztg.*, **35**, 1152 (1911).

[6] Bourion and Rouyer, *Ann. ch.*, [10] **10**, 263–355 (1928); cf. 5, *c*, Linhart.

"halomercuriates," e.g., Na_2HgCl_4, with various halides.[1] Consequently it gives in many cases what appear to be anomalous reactions. $HgCl_2$ is not decomposed by H_2SO_4, a compound is formed that distils undecomposed.

Hydrobromic acid and soluble bromides precipitate from solutions of mercurous salts, mercurous bromide, Hg_2Br_2, white, insoluble in water (5, *c*) and dilute HNO_3; NH_4OH converts it to $NH_2HgBrHgO \cdot 2H_2O$;[2] from concentrated solutions of mercuric salts, white mercuric bromide, $HgBr_2$, soluble in excess of mercuric salts or of the reagent. Sulfuric acid does not decompose $HgBr_2$ but forms a compound analogous to that with $HgCl_2$; excess of concentrated H_2SO_4 is said to give, however, some Br_2.[3]

Hydriodic acid and soluble iodides, precipitate from mercurous solutions, greenish-yellow[4] mercurous iodide, Hg_2I_2, insoluble in water and dilute HNO_3; insoluble in alcohol (distinction from HgI_2), soluble in $Hg_2(NO_3)_2$ and $Hg(NO_3)_2$; decomposed by excess reagent into Hg° and HgI_4^{--}. Hg_2Cl_2 is transposed to Hg_2I_2 by soluble iodides, excess of the reagent acting as above. NH_4OH converts Hg_2I_2 into $HgI_2 \cdot 2NH_3 + Hg^\circ$.[5]

Mercuric iodide, HgI_2, is obtained upon addition of an iodide to a mercuric solution. The unstable pale yellow HgI_2 first formed rapidly changes to the stable red modification,[6] insoluble in cold water;[7] fairly soluble in concentrated HCl (without decomposition) which is one of the best agents for recrystallizing HgI_2. Mercuric iodide is soluble in excess of iodide, giving complexes, e.g., Na_2HgI_4; such solutions do not give the normal reactions of Hg^{++} salts. This or the potassium salt, as Thoullet's reagent, is used for the determination of refractive index in mineralogy. In presence of excess fixed alkali, HgI_4^{--} is called Nessler's reagent and is used to detect NH_3, with which it gives a yellow to brown precipitate, the

[1] Idem.; *Compt. rend.*, **178**, 86–8 (1924); **182**, 1546–9 (1926); Yajnik and Uberoy, *J. Am. Ch. Soc.*, **46**, 802 (1924).

[2] Saha and Choudhuri, *Z. anorg. allgem. Ch.*, **77**, 41 (1912).

[3] For action of NH_4OH on $HgBr_2$ see Gaudechon, *Compt. rend.*, **148**, 1763 (1909); **150**, 467 (1910).

[4] François, *Compt. rend.*, **122**, 193 (1896); *J. Pharm. Ch.*, [6] **20**, 67 (1904).

[5] Saha and Choudhuri, *Z. anorg. allgem. Ch.*, **77**, 41 (1912).

[6] The red form is stable below 127°, the yellow form above 127° at atmospheric pressure.

Ostwald's generalization: When a substance leaves any state and passes into another more stable one, the one actually produced is not the most stable one under the existing conditions, but the one that can be reached with the minimum loss of free energy, e.g., with HgI_2, the yellow, unstable form first appears because it involves the minimum loss of free energy.

For the theory of allotropic states of HgI_2 see Smits, *Z. physik. Ch.*, **76**, 437 (1911), **82**, 657 (1913), **84**, 250, 385 (1913).

Hasselblatt, *Ibid.*, **86**, 61 (1913).

Tammann, *Ibid.*, **83**, 728 (1913); **84**, 753 (1914).

[7] The solubility data are very discordant "because the solubility is too small to estimate accurately"; Dunningham, *J. Ch. Soc.*, **105**, 733 (1914).

iodide of Millon's base, (see 6, *a*).[1] Mercuric iodide is not attacked by H_2SO_4 in the cold but when heated the salt is decomposed; salts analogous to $HgSO_4 \cdot 2HCl$ and $HgSO_4 \cdot 2HBr$ are not obtained. Mercuric iodide is soluble in $Na_2S_2O_3$ (the solution upon heating gives red HgI_2); soluble in concentrated HNO_3 (sp. g. 1.4–1.5) with formation of $Hg(IO_3)_2$; with more dilute acid $HgI_2 \cdot Hg(NO_3)_2$, white, separates on cooling.[2] If HgI_2 is boiled with alkali or alkaline earth hydroxides [not $Mg(OH)_2$], HgO and the complex M_2HgI_4 are obtained.[3] HgI_2 is soluble in ammonium salts, e.g., NH_4NO_3, $(NH_4)_2SO_4$, $(NH_4)_2CO_3$; moderately soluble in $HgCl_2$, $Hg(C_2H_3O_2)_2$ or $Hg(NO_3)_2$, NaCl, $CaCl_2$, $BaCl_2$, etc.; readily soluble in NaBr; transposed by KCN giving $Hg(CN)_2$ and 2 KI; decomposed by $SnCl_2$ forming finally Hg° and Sn^{+4}: $2\ HgI_2 + 2\ SnCl_2 = 2\ Hg^\circ + SnI_4 + SnCl_4$. For the action of NH_4OH on HgI_2 see 6, *a*.[4]

Excess of a soluble iodide acting on HgI_2 is said to give complexes: $MHgI_3$, M_2HgI_4, etc., of which M_2HgI_4 is most stable.[5] HgI_2 is reduced by alkali arsenites;[6] mercurous nitrate forms Hg_2I_2 and $Hg(NO_3)_2$.[7]

Potassium bromate (and $HBrO_3$) precipitates from solutions of $Hg_2(NO_3)_2$, mercurous bromate, $Hg_2(BrO_3)_2$, white; changes to the yellow basic salt upon heating in water; soluble in HCl with formation of $HgCl_2$; difficultly soluble in HNO_3. Mercuric nitrate yields, when treated with $KBrO_3$, mercuric bromate, $Hg(BrO_3)_2$, yellowish; soluble in 650 parts of cold and 64 parts of boiling water; slightly soluble in HNO_3; easily decomposed by HCl.[8] No precipitate is obtained when bromate is added to $HgCl_2$ due to the low $[Hg^{++}]$. Iodic acid and soluble iodates precipitate from $Hg_2(NO_3)_2$ solution, white mercurous iodate, $Hg_2(IO_3)_2$, difficultly soluble in water; not affected by boiling water or cold HNO_3. Mercuric iodate, $Hg(IO_3)_2$, obtained when KIO_3 is added to $Hg(NO_3)_2$, is white; it is completely converted to HgI_2 and O_2 upon heating; soluble in HI or HBr with release of I or Br; slightly soluble in solutions of alkali chlorides, bromides, iodides, cyanides or thiosulfates, HCl, or dilute solutions of $MnCl_2$ or $ZnCl_2$; insoluble in solutions of NaOH, Na_2CO_3, NH_4OH,

[1] The test can be reversed, of course, for the detection of Hg, Vogelenzang, *Pharm. Weekblad*, **66**, 65–7 (1929); *C.A.* **23**, 1591.

[2] See however: Luczizky, *Z. Kryst. Min.*, **46**, 297 (1909), who says that HgI_2 can be crystallized from hot HNO_3.

[3] Berthemot, *J. pharm.*, **14**, 186 (1828).

[4] Also Franklin, *Am. Ch. J.*, **47**, 373 (1912).

[5] For detailed discussion see Mellor, IV, 925–942.
For double salts of HgI_2 see Duboin, *Ann. ch. phys.* [8] **16**, 258 (1909).

[6] Kohn, *Z. anorg. allgem. Ch.*, **59**, 108 (1908).

[7] François, *J. Pharm. Ch.*, [6] **6**, 447 (1897); **22**, 97 (1905); *Compt. rend.*, **140**, 861 (1905).

[8] Rammelsberg, *Pogg. Ann.*, **55**, 79 (1842).

Na_2SO_3, $Na_2B_4O_7$, $HgCl_2$, Na_2HPO_4, alkali chlorate, bromate or iodate, $HC_2H_3O_2$ or HF.[1] $HgCl_2$ gives no precipitate with iodates.[2]

g. Arsenious acid and arsenites give a yellowish-white precipitate ($3Hg_2O \cdot As_2O_3$) with $Hg_2(NO_3)_2$, soluble in HNO_3, intensely yellow when air dried.[3] If $HgCl_2$ is treated with sodium arsenite a white precipitate of $3HgO \cdot As_2O_3$ is obtained. It turns yellow upon standing and is slightly soluble in water.[4] (The yellow color may be due to oxidation of some of the arsenite to arsenate.) Arsenic acid or Na_2HAsO_4 gives, with mercurous salts, a yellow to orange precipitate, insoluble in water.[5] With mercuric salts (not $HgCl_2$) yellow, mercuric orthoarsenate, $Hg_3(AsO_4)_2$, is obtained, slightly soluble in H_2O; readily in HCl.[6]

Stannous chloride precipitates from solutions of mercuric salts, white Hg_2Cl_2; if an excess of reagent be added Hg° is obtained. (This reaction is used as a final test for Hg^{++}.)

h. Soluble chromates or dichromates give with $Hg_2(NO_3)_2$ a precipitate of mercurous chromate, Hg_2CrO_4, the color is yellow to brown, even reddish depending upon conditions;[7] less soluble in chromate solution than in water; soluble in HNO_3. Mercuric nitrate is precipitated by soluble chromates as a light yellow precipitate, rapidly darkening in color; readily soluble in acids and $HgCl_2$. Mercuric chloride forms a precipitate with normal chromates, but not with $K_2Cr_2O_7$.

7. Ignition. — All mercury compounds are volatilized by heat with or without decomposition. Hg_2Cl_2 vaporizes as such if dry but in the presence of moisture decomposes to form Hg° and $HgCl_2$.[8] Mercuric chloride volatilizes undecomposed as does Hg_2Br_2, $HgBr_2$,[9] Hg_2I_2 (if carefully heated) and HgI_2 (overheating gives $Hg + I_2$). Most other compounds of Hg are decomposed by vaporization, and give a sublimate of Hg° (mixed with S if from the sulfide, etc.). All compounds of Hg, dry and intimately mixed with dry Na_2CO_3 and heated in a test tube, give a sublimate of Hg° as a gray coating on the inner surface of the cold part of the tube. Magnified, the coating is seen to consist of globules which by gentle rubbing with a glass rod or a wire will flow together forming a larger drop visible to the unaided eye.

8. Detection.[10] — *a.* Mercury in the lower valence belongs to the first group, and is completely precipitated by HCl. It is separated from $PbCl_2$ (and TlCl), which is soluble in hot H_2O, and identified by means of NH_4OH, which changes the white Hg_2Cl_2 to black (gray) NH_2Hg_2Cl (NH_2HgCl +

[1] Cameron, *Ch. News*, **33**, 253 (1876).

[2] *Idem.*

[3] Reichard, *Ch. Ztg.*, **26**, 1143 (1902).

[4] *Idem.*

[5] Haack, Inaug. Dissert., Halle, **1890**, p. 35; *Ann.*, **262**, 190 (1891).

[6] *Idem.*

[7] Fichter and Oesterheld, *Z. anorg. allgem. Ch.*, **76**, 350 (1912).

[8] Cf. Smith and Menzies, *J. Am. Ch. Soc.*, **32**, 1541 (1910).

[9] Beckmann, *Z. anorg. allgem. Ch.*, **55**, 182 (1907); Prideaux, *J. Ch. Soc.*, **97**, 2032 (1910).

[10] Gutzeit, *Helv. Ch. Acta*, **12**, 713–40 (1929); *C.A.* **23**, 4644, has summarized the characteristic tests for Hg.

Hg°). This is a delicate and specific test for Hg_2Cl_2. Mercury in the mercuric state is not precipitated by HCl (separation and distinction from Hg_2^{++}), but forms a sulfide (HgS) insoluble in dilute acid solution, hence belongs in the second group. The separation of Hg^{++} from all other metals of that group is based upon the insolubility of HgS in $(NH_4)_2S_x$ (separation from As division), and in HNO_3 (2 *N*) (separation from other metals of Cu division). The sulfide is dissolved in aqua regia or HCl + $KClO_3$ and the presence of Hg confirmed by addition of $SnCl_2$[1] giving Hg_2Cl_2 (white) or Hg° or a mixture of both (gray in color).

If a piece of copper is placed in a solution of a mercury salt Hg° will deposit on the metal giving it a gray appearance which upon polishing becomes silvery. (A good test for Hg, but it will not differentiate the two valences.[2]) Selenium sulfide will detect one part of Hg in four million of air on a four-minute exposure.[3]

b. Organic Reagents. — (1) An alcoholic solution of diphenylcarbazide added to a neutral or slightly acid solution containing mercurous ions gives a blue-violet color. The test is very sensitive but is masked by Cu and inhibited by Zn. Mercuric ions give the same test.[4]

(2) Diphenylthiocarbazide gives with ions of Hg an ochre yellow changing to red upon addition of HCl.[5]

9. Determination. — *Gravimetrically,* mercury may be separated and weighed as the sulfide, HgS, or the metal. (a) The sulfide method involves the precipitation of HgS in acid solution, digestion with dilute HNO_3 to remove other sulfides, solution in aqua regia and reprecipitation as HgS from ammoniacal tartrate solution. The precipitate thus obtained is carefully dried and weighed. Another way is to reduce the mercury to Hg° by means of hydrazine or hydroxylamine in ammoniacal tartrate solution. The dark gray precipitate, free from other metals (not Ag), is dissolved in HNO_3, NH_4CNS or tartrate added, then excess NH_4OH and finally H_2S giving HgS which is washed, dried and weighed. (b) All mercury compounds when ignited with Na_2CO_3 are decomposed giving volatile Hg°. This may be collected on a silver or gold foil and weighed.[6] Neutral or slightly acid solutions of Hg_2^{++} or Hg^{++} may be electrolyzed and the Hg° deposited on a Pt gauze or in a Pt dish used as a cathode.

Mercurous salts may be precipitated as Hg_2Cl_2 but should not be weighed as such due to the danger of loss from volatilization while drying. Mercuric salts may also be precipitated as Hg_2Cl_2 after reduction with H_3PO_3 or H_3PO_2 (in presence of H_2O_2 to prevent further reduction to Hg°).

[1] Górski, *Z. anorg. allgem. Ch.*, **81**, 315 (1913), has studied the sensitivity of the $SnCl_2$ test.

[2] Various modifications of this test and others have been proposed to increase the delicacy. Concerning the general situation see Noyes and Bray, *J. Am. Ch. Soc.*, **29**, 137 (1907). Some refinements are:

(1) deposition on a Cu wire giving a sensitivity of one in a billion; Booth and Schreiber, *J. Am. Ch. Soc.*, **47**, 2625 (1925); (2) use of aluminum; Denis, *Ann. méd. légale*, **1**, 348 (1929); *C.A.* **20**, 1365.

[3] Nordlander, Brit. Pat. 264,820; *C.A.* **22**, 188.

[4] Cazeneuve, *Compt. rend.*, **130**, 1478, 1561 (1900); **131**, 346 (1900).
Parri, *Giorn. farm. ch.*, **73**, 207 (1924); cf. Scott, *J. Am. Ch. Soc.*, **51**, 3351–2 (1929).

[5] Kolthoff, *Ch. Weekblad*, **21**, 20 (1924).

[6] Holloway Eschka process.

Volumetrically, mercury may be determined (a) by reduction to Hg° in NaOH solution with excess standard arsenite solution, the excess being determined with iodine; (b) by titration with standard thiocyanate (halogens and CN^- absent) using ferric alum as indicator.[1]

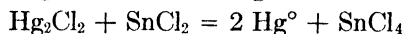
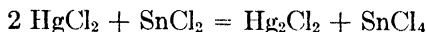
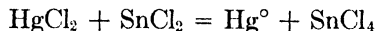
10. Oxidation and Reduction. — Free mercury precipitates Ag, Au and Pt from their solutions, and reduces Hg^{++} to Hg_2^{++}. Potassium permanganate in the cold oxidizes the metal to Hg_2O, when hot to HgO. Metallic Hg and Hg_2^{++} are oxidized to Hg^{++} by Br, Cl, I, HNO_3, H_2SO_4 (concentrated and hot) and $HClO_3$.

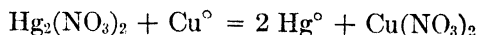
Reducing agents, as Pb, Sn, Sn^{++}, Bi, Cu, Cu_2^{++}, Cd, Al, Fe, Co, Zn, Mg, H_3PO_2, H_3PO_3 and H_2SO_3, precipitate, from solutions of mercurous and mercuric nitrates, gray Hg°; from solutions of mercuric chloride, or in the presence of Cl^-, first the white Hg_2Cl_2, then gray Hg°. Concentrated HNO_3 interferes with the reduction, while heating promotes it.

The reducing agent most frequently employed is stannous chloride:

$$2\,HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4$$
$$Hg_2Cl_2 + SnCl_2 = 2\,Hg^{\circ} + SnCl_4$$

or

$$HgCl_2 + SnCl_2 = Hg^{\circ} + SnCl_4$$

A clean strip of copper, placed in a slightly acid solution of Hg_2^{++} or Hg^{++} becomes coated with metallic mercury, and when gently rubbed with cloth or paper presents the tin-white luster of the metal:

$$Hg_2(NO_3)_2 + Cu^{\circ} = 2\,Hg^{\circ} + Cu(NO_3)_2$$

The coating is driven off by heat. Formic acid reduces Hg^{++} to Hg_2^{++} and in the cold does not effect further reduction. Dry $HgCl_2$, moistened with alcohol, is reduced by metallic iron, a bright strip of which is corroded soon after immersion in the sample to be tested (distinction from Hg_2Cl_2).

§59. Silver (Anglo-Sax., soelfor) (Argentum). Ag = 107.880. Valence 1. Atomic No. 47. Discovery prehistoric.

1. Physical Properties. — Density, 10.493 at 0°/4°, (vacuum redistilled);[2] melting point, 960.5°;[3] boiling point, 1944° (calc.).[4] It is the whitest of the metals, harder than gold and softer than copper, (2.7 on Moh's scale[5]). As a vapor or in very thin layers Ag has a blue to violet color; when molten it is luminescent and absorbs oxygen, also

[1] Rupp, *Ch. Ztg.*, **32**, 1077 (1908).
[2] Stahl, *Metall. u.Erz.*, **19**, 213 (1922).
[3] B. Stds. *Cir.* **35**; Auerbach, *Z. angew. Ch.*, **38**, 449 (1925).
[4] Van Liempt, *Z. anorg. allgem. Ch.*, **114**, 105 (1920).
[5] Rydberg, *Z. physik. Ch.*, **33**, 353 (1900).

phosphorus, but not H_2 or N_2.[1] At the melting point and 760 mm., one volume of Ag° absorbs over 20 volumes of O_2.[2] Upon solidification the oxygen is released, giving rise to the characteristic "spitting." In malleability and ductility, Ag is inferior only to gold; as a conductor of heat and electricity it is superior to all other metals. United States coin silver contains 90% Ag + 10% Cu (as a hardener). Other uses for silver are for silver-ware, silver plating, and photographic supplies.

2. Occurrence. — Silver is frequently found in the free state, occasionally as large masses. (In Peru lumps have been found weighing over 800 lbs.) The chief silver ores are argentite, or silver glance, Ag_2S; pyrargyrite, Ag_3SbS_3; and horn silver, AgCl. In addition, silver is frequently found as a minor constituent of other ores, e.g., copper ores of the United States contribute over 25% of our silver, lead ores yield about the same, and lead-zinc ores over 10%. The world production in 1927 was over 252 million ounces, valued at $142,000,000, viz. 56¢ per ounce.[3] Mexico is the leading silver country, producing about 40% of the world's supply; the United States — chiefly Montana — produces 23%. India and China are the largest consumers of Ag.

3. Preparation. — Silver is one of the most easily reduced of the metals; the difficulties that attend its winning are all due to the fact that the percentage of Ag is small, hence concentration methods of one sort or another are necessary. (a) Silver is obtained as a by-product from copper ores. It goes along with the Cu through the various metallurgical processes down to the electrolytic refining of the Cu. There the Ag is left behind in the " anode sludge " along with the other precious metals, from which it may be separated by a variety of methods. (b) Ag as a by-product in lead ores is removed by adding Zn to the molten metal. (Ag is about 3000 times more soluble in Zn than in Pb, and Zn is insoluble in Pb.) The Zn is separated from the Ag by distillation, the former being readily volatile at about 900° (Parke's process). (c) Recovery of silver is also effected by leaching the ores with solutions such as NaCN, $Na_2S_2O_3$, or NaCl. This is followed by removal of the Ag from the extract electrolytically or otherwise.[4]

4. Oxides and Hydroxides. — Ag_2O, Ag_2O_2, $[Ag_2O_3 \cdot AgO]$. Silver oxide, Ag_2O, brown, is formed by the action of alkali hydroxides on silver salts or by heating the carbonate to 200°. It is decomposed into Ag° and O_2 at 300°. Silver peroxide, Ag_2O_2 $[Ag_2O_3 \cdot AgO]$, black, is obtained when $AgNO_3$ is treated with a persulfate: $Ag_2S_2O_8 + 2\,H_2O = Ag_2O_2 + 2\,H_2SO_4$.[5] This compound is a very active oxidizing agent. Other oxides of Ag have been reported (Ag_4O, Ag_3O_4, Ag_4O_3), but their existence has been questioned.[6]

5. Solubilities. — *a. Metal.* — The best solvent for Ag° is HNO_3 (2 : 1), containing a little nitrite,[7] in the absence of which the reaction is very sluggish: $Ag^\circ + 2\,HNO_3 = AgNO_3 + H_2O + NO_2$. Ag° is soluble in concentrated H_2SO_4 (80%), especially when hot:[8] $Ag + 2\,H_2SO_4 = Ag_2SO_4 + SO_2 + 2\,H_2O$. (The presence of dissolved O_2 is necessary according to Hendrixson.[9]) HCl (1.18), is without action on pure Ag°; HI reacts with evolution of hydrogen. $HClO_3$, $HBrO_3$ and HIO_3 all act on Ag°: $6\,Ag^\circ + 6\,HClO_3 = AgCl + 5\,AgClO_3 + 3\,H_2O$.[10] Free halogens, if dry, have slight action at ordinary temperatures;[11] at higher temperatures the Ag° may be completely converted

[1] Sieverts and Krumbhaar, *Ber.*, **43**, 893 (1910).

[2] Sieverts and Hagenacker, *Z. physik. Ch.*, **68**, 116 (1909); compare Donnan and Shaw, *J. Soc. Ch. Ind.*, **29**, 987 (1910).

[3] In 1930, silver sold for less than 30¢ per ounce.

[4] Evans, IV, 86.

[5] Lüppo-Cramer, *Z. Ch. Ind. Kolloide*, **2**, 171 (1907); Austin, *J. Ch. Soc.*, **99**, 262 (1911); Higson, *Ibid.*, **119**, 2048–55 (1921). Concerning the nature of Ag "peroxide," however, see Barbieri, *Atti. accad. Lincei*, II, **16**, 72–9 (1907).

[6] For bibliography on lower oxides of Ag, see: Jirsa, *Ch. Listy*, **19**, 300 (1926); *Z. anorg. allgem. Ch.*, **148**, 130 (1925).

[7] Stansbie, *J. Soc. Ch. Ind.*, **32**, 311 (1913).

[8] Pannain, *Gazz. ch. ital.*, **39**, II, 234 (1909).

[9] Hendrixson, *J. Am. Ch. Soc.*, **25**, 637 (1903).

[10] Hendrixson, *Ibid.*

[11] Cf. Reboul, *Compt. rend.*, **156**, 548 (1913).

to silver halide.[1] Ag° is not affected by acetic acid; is tarnished by H_2S (pure dry H_2S is without action[2]), soluble sulfides, and many organic compounds containing sulfur. At ordinary temperatures, silver is not affected by moisture or atmospheric oxygen, but at 200° a slight film of Ag_2O is formed.[3] The metal is not acted upon by fixed alkalis, hence the use of Ag crucibles for caustic fusions. When finely divided, silver is dissolved by NH_4OH in the presence of O_2.[4]

b. Oxides. — Silver oxide, Ag_2O, dissolves in water to the extent of 0.02 g. per liter.[5] It combines with nearly all acids (not H_2CO_3), forming the corresponding salts. The peroxide acts similarly, with reduction where possible. AgOH has not been isolated.

c. Salts. — Ag forms a greater number of insoluble salts than any other known metal, though in this respect it is approached by Pb and Hg. The solubility of the commoner salts is as follows:

TABLE 34

SOLUBILITY* OF SILVER SALTS

Salt	$t°$	Solubility in g./100 g. H_2O	Salt	$t°$	Solubility in g./100 g. H_2O
Acetate	20	1.04	Fluoride	20	172.
Arsenate†	..	0.0_385	Iodate	25	0.00503
Arsenite	..	.00115	Iodide	..	$.0_628$
Borate	25	.905	Nitrate	18	216.
Bromate	25	.196	Oxalate	21	0.00378
Bromide	25	$.0_414$	Oxide	18	.00248
Carbonate	25	.105	Phosphate	20	$.0_364$
Chloride	21	$.0_3154$	Sulfate	25	.83
Chromate	18	.00256	Sulfide	..	$.0_4174$
Cyanide	20	$.0_422$	Tartrate	18	.0201
Ferricyanide	20	0_466	Thiocyanate	21	$.0_425$

* Additional data are to be found in the following sources: Whitby, *Z. anorg. allgem. Ch.*, **67**, 107–9 (1910); Seidell, "Solubility of Inorganic and Organic Compounds," D. Van Nostrand Company, New York, **1919** and **1928**.

† The names refer to the normal salts, e.g., arsenate = Ag_3AsO_4.

Silver chloride is appreciably soluble in HCl and other chlorides, due to the formation of a complex argentichloride, e.g., H_2AgCl_3, H_3AgCl_4.[6] For analytical work, AgCl is probably most insoluble in 0.0025 N chloride solution.[7] Concentrated HNO_3 has slight effect upon AgCl. Concen-

[1] Kastle, *Am. Ch. J.*, **45**, 396 (1911).

[2] Cabell, *Ch. News*, **50**, 208 (1884).

[3] Manchot, *Ber.*, **42**, 3942 (1909); cf. Krepelka and Toul, *Collection Czechoslav. Ch. Comm.*, **1**, 155–64 (1929); *C.A.* **23**, 3616.

[4] Hofmann and Hofmann, *Ber.*, **61B**, 2566–75 (1928); *C.A.* **23**, 1361.

[5] Whitby, *Z. anorg. allgem. Ch.*, **67**, 107 (1910).

[6] Solubility of AgCl in HCl at 21°:

1% HCl – 0.2 mg./l.
5% HCl – 3.3 mg./l.
10% HCl – 74.0 mg./l.

[7] Forbes and Cole, *J. Am. Ch. Soc.*, **43**, 2492 (1921); cf. Forbes, *J. Am. Ch. Soc.* **33**, 1937 (1911).

trated H_2SO_4 (density 1.84), completely transposes even the fused chloride on long boiling (due to removal of Cl^- as gaseous HCl). AgCl is soluble in NH_4OH, $(NH_4)_2CO_3$ and $Hg(NO_3)_2$ ($HgCl_2$ is very slightly ionized). Of the silver salts insoluble in water, NH_4OH dissolves all except Ag_2S and AgI;[1] $(NH_4)_2CO_3$ all except AgBr, AgI, Ag_2S, (the bromide being very slightly soluble); cold, dilute HNO_3 dissolves all except AgCl, AgBr, $AgBrO_3$, AgI, $AgIO_3$, AgCN and AgCNS; NaCN (and many other cyanides), all except Ag_2S;[2] and alkali thiosulfates dissolve all.[3] Silver nitrate is very soluble in water, soluble in glycerol, sparingly soluble in alcohol or ether.

6. Reactions. — *a.* The fixed alkali or alkaline earth hydroxides precipitate, from solutions of Ag^+, silver oxide, Ag_2O, grayish brown,[4] insoluble in excess of the reagent; soluble in acids, alkali cyanides, thiosulfates, ammonium salts and NH_4OH.

Caution!! Do not dissolve Ag_2O in NH_4OH in the absence of ammonium salts because of possible formation of the highly explosive "fulminating silver," (NAg_3 or $NAgH_2$). It will explode when only slightly jarred.[5] Most silver salts, the iodide excepted, are transposed on boiling with the fixed alkalis. Silver oxide is strongly basic, decomposed by light and heat, and somewhat soluble in H_2O (see above). With carbon tetrachloride, CCl_4, phosgene, $COCl_2$, (very poisonous) is formed:[6] $Ag_2O + CCl_4 = 2\ AgCl + COCl_2$.

Ammonium hydroxide in neutral solutions of Ag^+ forms a precipitate of Ag_2O, readily soluble in excess of the reagent:[7] $AgNO_3 + 2\ NH_4OH = Ag(NH_3)_2NO_3 + 2\ H_2O$. In solutions initially containing much free acid no precipitate is obtained due to the large amount of NH_4^+ formed, which represses the ionization of the NH_4OH and thus lowers the concentration of OH^-.

Alkali carbonates or bicarbonates[8] precipitate silver carbonate, Ag_2CO_3, white to yellowish white. Generally some Ag_2O is also obtained. Upon heating, Ag_2CO_3 commences to decompose around 150°[9] with formation of Ag_2O. Silver carbonate is readily soluble in NH_4OH and $(NH_4)_2CO_3$,

[1] $[Ag^+]$ from $(NH_3)_2Ag^+$ is lower than that from the salt. See Stieglitz, I, 216, for a more complete discussion.

[2] Due to the formation of a complex negative ion, $Ag(CN)_2^-$, in which the concentration of the Ag^+ is less than in other salts. Ag_2 is slightly soluble in excess.

[3] Ag_2S is soluble in excess, forming a complex. See Gmelin-Kraut, 7th ed., V, 2, p. 74.

[4] In the presence of citrate or tartrate, the precipitate is almost white.

[5] Sieverts, *Z. angew. Ch.* **22**, 6 (1909); Olmer, *Bull. soc. ch.*, [4] **35**, 847 (1924).

[6] Michael and Murphy, *Am. Ch. J.*, **44**, 365 (1910).

[7] For formula of the complex, see: Straub, *Z. physik. Ch.*, **77**, 331 (1911); Bruni and Levi, *Gazz. ch. ital.*, **46**, II, 17 (1916); Biltz and Stollenwerk, *Z. anorg. allgem. Ch.*, **114**, 174 (1920).

[8] Spencer and Le Pla, *Z. anorg. allgem. Ch.*, **65**, 11 (1909).

[9] Kohlschütter and Eydmann, *Ann.*, **398**, 5 (1913).

and is transposed by inorganic acids, forming the corresponding salts. Carbon dioxide does not transpose silver salts.

b. Oxalic acid and soluble oxalates precipitate Ag^+ as silver oxalate, $Ag_2C_2O_4$,[1] white, soluble in 22% HNO_3 to the extent of 18 g./l.,[2] difficultly soluble in H_2SO_4, readily soluble in NH_4OH, forming $[Ag(NH_3)_2]_2C_2O_4$. Heated under water, silver oxalate does not decompose; heated dry, it decomposes explosively to $Ag^\circ + CO_2$;[3] exposed to sunlight it partially decomposes.

Alkali cyanides precipitate from neutral or slightly acid solutions, silver cyanide, AgCN, white; insoluble[4] in water; readily soluble in excess of the reagent, forming the complex $Ag(CN)_2^-$;[5] soluble in NH_4OH and ammonium salts, e.g., $(NH_4)_2CO_3$, NH_4NO_3, $(NH_4)_2SO_4$; slowly soluble in hot, dilute HNO_3, with evolution of HCN. The same is true for H_2SO_4 and HCl. The ready solubility of nearly all silver compounds in alkali cyanide affords a means of separating silver from many minerals. It should be noted, however, that the action on Ag is much less rapid than on Au in the cyanide process for obtaining these metals.

Potassium ferrocyanide[6] precipitates silver ferrocyanide, $Ag_4Fe(CN)_6$, white. It is soluble in NH_4OH but not in ammonium salts. Boiling with NH_4OH produces complete decomposition: $Ag_4Fe(CN)_6 + 2\ NH_4OH = Fe(OH)_2 + 4\ AgCN + 2\ NH_4CN$.[7] According to Bloxam,[8] another reaction also takes place: $Ag_4Fe(CN)_6 + 3\ NH_4OH = 3\ AgCN + 3\ NH_4CN + Ag + Fe(OH)_3$. Boiling $Ag_4Fe(CN)_6$ alone yields Ag° and $Ag_3Fe(CN)_6$. Silver ferrocyanide is slowly decomposed by H_2SO_4, oxidized by HNO_3 to ferricyanide. Exposure to air results in slight oxidation of the Fe with the formation of some $Fe_4[Fe(CN)_6]_3$, which imparts a blue color to the silver salt. Potassium hydroxide promotes decomposition in the cold, the products being Ag° and $Ag_3Fe(CN)_6$.

Potassium ferricyanide precipitates silver ferricyanide, $Ag_3Fe(CN)_6$, reddish brown, becoming more yellowish and compact on heating. The precipitate is readily soluble in NH_4OH, decomposed by fixed alkalis to Ag_2O and $M_3Fe(CN)_6$ (see above), insoluble in water.

Soluble thiocyanates (except Hg^{++}) precipitate silver thiocyanate, AgCNS, white, insoluble in water, insoluble in slight excess of reagent or in HNO_3. A concentrated solution of the reagent readily dissolves

[1] *Idem.*, p. 9.

[2] Hill and Simmons, *J. Am. Ch. Soc.*, **31**, 827 (1909).

[3] V. Meyer, *Ber.*, **23**, 582 (1890).

[4] Böttger, *Z. physik. Ch.*, **46**, 602 (1903).

[5] Masaki, *Bull. Ch. Soc. Japan*, **4**, 190–3 (1929), *C.A.* **24**, 2078, states that the molal ratio of combined cyanide to Ag is 1 : 1 for AgCN, AgCl, AgCNS, Ag_2O, or Ag_2CrO_4.

[6] Cf. Bonino, *Gazz. ch. ital.*, **51**, II, 261 (1921).

[7] Weith, *Z. Ch.*, [2] **5**, 381 (1869).

[8] Bloxam, *Ch. News*, **48**, 73 (1883). Probably the reaction is not completely given by either equation.

AgCNS. It is reprecipitated upon dilution. Silver thiocyanate is readily soluble in NH_4OH, especially when warmed. Reprecipitation takes place on cooling, glistening colorless crystals being formed. AgCNS is decomposed by Cl or I. It is distinctly soluble in concentrated $AgNO_3$, forming $2AgNO_3 \cdot AgCNS$. Concentrated H_2SO_4, hot, dissolves AgCNS in the presence of excess $AgNO_3$ (separation from AgCl).

c. Silver nitrate is readily soluble in water,[1] but only slightly soluble in concentrated nitric acid.

TABLE 35

SOLUBILITY OF SILVER NITRATE IN NITRIC ACID

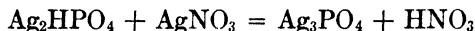
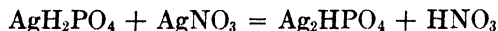
HNO_3%	0.0	18.4	38.8	72.3
$AgNO_3$	66.65*	23.8	8.9	1.3

* Grams of $AgNO_3$ per 100 g. of saturated solution at 15°. (Seidell, Suppl. p. 1405.)

Silver nitrite, $AgNO_2$, is slightly soluble in H_2O and readily oxidized by atmospheric oxygen to $AgNO_3$. In solutions of KNO_2 and $Ba(NO_2)_2$, complexes of the type $MAg(NO_2)_2 \cdot 0.5H_2O$, are formed.[2]

d. Silver hypophosphite[3] and silver phosphite[4] are of minor importance analytically. Disodium phosphate, Na_2HPO_4, gives a yellow precipitate with Ag^+, darkening on exposure to light. The composition of the precipitate approaches Ag_3PO_4, silver orthophosphate, but probably is a mixture of that compound with Ag_2HPO_4, the relative quantity of each depending upon conditions:[5]

1. $Na_2HPO_4 + AgNO_3 + HNO_3 = 2\ NaNO_3 + AgH_2PO_4$
   $AgH_2PO_4 + AgNO_3 = Ag_2HPO_4 + HNO_3$
   $Ag_2HPO_4 + AgNO_3 = Ag_3PO_4 + HNO_3$

2. $4\ Na_2HPO_4 + 9\ AgNO_3 = 3\ Ag_3PO_4 + 8\ NaNO_3 + HNO_3 + H_3PO_4$

The precipitate is soluble in acids, NH_4OH and $(NH_4)_2CO_3$; insoluble in water.

Sodium pyrophosphate, $Na_4P_2O_7$, precipitates white silver pyrophosphate, $Ag_4P_2O_7$. It has the same solubilities as the orthophosphate, except that it is insoluble in acetic acid.

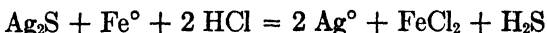
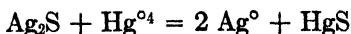
e. Hydrosulfic acid, H_2S, and soluble sulfides precipitate silver sulfide, Ag_2S, black. This compound is less soluble than AgI. It is soluble in

[1] Graulich, *Edel-Erden u.-Erze*, **3**, 2 (1921).
[2] Pick, Dissert., Breslau, **1906**, p. 27.
[3] Gutbier, *Z. anorg. allgem. Ch.*, **32**, 347 (1902); Das, *Ch. News*, **101**, 51 (1910); Mitchell, *J. Ch. Soc.* (Trans.), **123**, 629 (1923).
[4] Sänger, *Ann.*, **232**, 14 (1886).
[5] Lang and Kaufmann, *J. Am. Ch. Soc.*, **27**, 1515 (1905); Baxter and Jones, *Ibid.*, **32**, 298 (1910).

HNO_3 (over 5%) (distinction from Hg[1]), soluble in KCN:[2] $Ag_2S + 4\ KCN = 2\ KAg(CN)_2 + K_2S$;[3] insoluble in NH_4OH and alkali sulfides (distinction from As, Sb and Sn); converted by boiling with NaCl to AgCl (mass action effect). Certain insoluble sulfides, when boiled with $AgNO_3$ give Ag_2S: $CuS + 2\ AgNO_3 = Ag_2S + Cu(NO_3)_2$. The reaction of Ag_2S with certain metals is illustrated by the following equations:

$$Ag_2S + Hg^{\circ 4} = 2\ Ag^\circ + HgS$$

$$Ag_2S + Fe^\circ + \text{heat} = FeS + 2\ Ag^\circ$$

$$Ag_2S + Fe^\circ + 2\ HCl = 2\ Ag^\circ + FeCl_2 + H_2S$$

Ammonium thioacetate reacts with Ag^+ to give Ag_2S.

Sodium thiosulfate, $Na_2S_2O_3$, gives a white[5] precipitate of silver thiosulfate, $Ag_2S_2O_3$, readily soluble in excess of the reagent, forming double salts: $Ag_2S_2O_3 \cdot xNa_2S_2O_3$ (where x usually equals 1, 2 or 3).[6] The product is readily decomposed by warming with H_2O: $Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4$.

Sulfurous acid and soluble sulfites precipitate silver sulfite, Ag_2SO_3, white. It resembles precipitated AgCl, rapidly darkening on exposure to light. It is decomposed by excess of H_2SO_3 and is soluble in excess of alkali sulfite. Its solubility in water is less than 0.05 g./l.[7] There is some decomposition when Ag_2SO_3 is put into boiling water.[8] The precipitate is Ag°.[9] Silver sulfite is soluble in NH_4OH, from which solution Ag° is fairly readily precipitated. Treatment of Ag_2SO_3 with a strong acid liberates SO_2.

Sulfuric acid and soluble sulfates precipitate from concentrated solutions of silver salts, silver sulfate, Ag_2SO_4, white. The product is slightly soluble in H_2O,[10] more soluble in HNO_3; the solubility is increased by H_2SO_4, decreased by K_2SO_4.[11] Silver sulfate reacts with Fe^{++} to give Ag°: $Ag_2SO_4 + 2\ FeSO_4 = 2\ Ag^\circ + Fe_2(SO_4)_3$. At 0° the reaction with bromine is: $Ag_2SO_4 + 2\ Br_2 + 2\ H_2O = 2\ AgBr + 2\ H_2SO_4 + 2\ HBrO$.

[1] Gruener, *J. Am. Ch. Soc.*, **32**, 1030 (1910).

[2] Kühn, *Metall.*, **8**, 434, 464 (1911).

[3] Göpner, *Ibid.*, **6**, 134 (1909); cf. Lucas, *Z. anorg. allgem. Ch.*, **41**, 193 (1904).

[4] If the Hg° is in excess an amalgam is formed.

[5] Usually gray due to the presence of a little Ag_2S.

[6] Cf. Jonsson, *Ber.*, **54B**, 2556 (1921).

[7] Baubigny, *Compt. rend.*, **149**, 858 (1909).

[8] Bodnár, *Z. anal. Ch.*, **53**, 39 (1914).

[9] Baubigny, *loc. cit.*, says that $Ag_2S_2O_6$ is obtained to the extent of 80%: $2\ Ag_2SO_3 \rightarrow Ag_2S_2O_6 + 2\ Ag^\circ$.

[10] Euler, *Z. physik. Ch.*, **49**, 314 (1904); cf. Barre, *Ann. ch. phys.*, [8] **24**, 145 (1911); Harkins, *J. Am. Ch. Soc.*, **33**, 1812 (1911).

[11] Harkins, *loc. cit.*

When heated the oxidation is more vigorous: $5\ Ag_2SO_4 + 6\ Br_2 + 6\ H_2O = 10\ AgBr + 5\ H_2SO_4 + 2\ HBrO_3$.[1]

Alkali persulfates give, with Ag^+, first $Ag_2S_2O_8$, which in the presence of H_2O, decomposes to Ag_2O_2 and H_2SO_4.[2]

f. Chlorine, bromine and iodine, when added to a solution of Ag^+, form the corresponding halide and halate, the hypohalite being an intermediate product: $6\ AgNO_3 + 3\ Br_2 + 3\ H_2O = 5\ AgBr + AgBrO_3 + 6\ HNO_3$.[3] Hydrofluoric acid[4] does not give a precipitate of silver fluoride. The dry salt, prepared otherwise, will absorb over 800 times its volume of NH_3. This fluoride is readily affected by light. Hydrochloric acid and soluble chlorides precipitate silver chloride, AgCl, curdy, white. The precipitate is made more compact and easy to filter by vigorously shaking the mixture. Silver chloride turns violet to brown on exposure to light. It is fusible without decomposition, is insoluble in water, slightly more soluble in HNO_3, insoluble in low concentrations of HCl and other highly ionized chlorides, but slightly soluble in more concentrated solutions due to the formation of a complex ion, $AgCl_3^{--}$.[5] Silver chloride is soluble in NH_4OH, forming $Ag(NH_3)_2Cl$.[6] If mercurous chloride is present in excess, little if any AgCl will go into solution, since the reaction between Hg_2Cl_2 and NH_4OH produces Hg°, which displaces the Ag, forming Ag°, insoluble in NH_4OH. Silver chloride is soluble in $Na_2S_2O_3$, forming a double salt.[7] It is soluble in alkali cyanides, the ion $Ag(CN)_2^-$ giving a lower concentration of Ag^+ than does AgCl. It is fairly soluble in $Hg(NO_3)_2$. If HCl is added to a mixture of $AgNO_3$ and $Hg(NO_3)_2$ (the latter in excess), no precipitate of AgCl may be obtained, since $HgCl_2$ in the presence of excess $Hg(NO_3)_2$, gives a lower concentration of Cl^- than AgCl, even though AgCl is so insoluble. Hence, upon addition of the HCl, all of the chloride ions are appropriated by the mercuric ions.[8]

Soluble sulfides convert AgCl to Ag_2S. Many metals, in the presence of HCl or H_2SO_4, reduce AgCl to Ag°, e.g., Zn, Cd, Fe, Al, etc. Potassium ferrocyanide converts AgCl into $AgK_3Fe(CN)_6$, (AgBr and AgI are not affected).[9] Cold, dilute H_2SO_4 does not affect AgCl; the hot con-

[1] Normand and Cumming, *J. Ch. Soc.*, **101**, 1855 (1912).

[2] Austin, *J. Ch. Soc.*, **99**, 262 (1911); Higson, *Ibid.*, **119**, 2048 (1921).

[3] Taylor, *J. Ch. Soc.*, **103**, 31 (1913); Normand and Cumming, *loc. cit.*, p. 1852.

[4] Cf. Guntz and Guntz, *Ann. ch.* **2**, 101 (1914).

[5] Forbes, *J. Am. Ch. Soc.*, **33**, 1946 (1911); cf. Riesenfeld and Feld, *Z. Elektroch.*, **26**, 282 (1920). Forbes and Cole, *J. Am. Ch. Soc.*, **43**, 2492 (1921), calculated that AgCl should have a minimum solubility in 0.0025 *N* chloride and that in the lower concentrations of chloride ion $AgCl_2^-$ is formed.

[6] Straub, *Z. physik. Ch.*, **77**, 331 (1911); cf. Biltz and Stollenwerk, *Z. anorg. allgem. Ch.*, **114**, 174 (1920).

[7] Richards and Faber, *Am. Ch. J.*, **21**, 167 (1899); Rosenheim and Steinhäuser, *Z. anorg. allgem. Ch.*, **25**, 103 (1900).

[8] Hewitt, *J. Ch. Soc. (Proc.)*, **23**, 10 (1907); Finzi, *Gazz. ch. ital.*, **32**, II, 324 (1902).

[9] Bonino, *Gazz. ch. ital.*, **51**, II, 261 (1921).

centrated acid converts $AgCl$ to Ag_2SO_4 with evolution of HCl. HBr converts $AgCl$ to $AgBr$ with difficulty, while HI readily forms AgI.

The precipitation of Ag^+ by HCl, excess $Hg(NO_3)_2$ being absent, is the most delicate of the ordinary tests for Ag^+, one part in 3–5 million parts of H_2O being recognizable.[1,2] Since Hg^{++} is not precipitated by HCl and Pb^{++} is incompletely separated, silver is the only metal that belongs exclusively to the First or Silver Group.

Hydrobromic acid and soluble bromides precipitate very light yellow silver bromide, $AgBr$, insoluble in H_2O,[3] slightly soluble in alkali bromides, much less soluble in NH_4OH than $AgCl$, soluble in $Na_2S_2O_3$, moderately soluble in NH_4CNS. Ferrous sulfate in sunlight is without action on $AgBr$; boiling HNO_3 has no effect; hot H_2SO_4 causes decomposition: $2\ AgBr + 2\ H_2SO_4 = Ag_2SO_4 + SO_2 + Br_2 + 2\ H_2O$.

Hydriodic acid and soluble iodides precipitate silver iodide, AgI, yellow, insoluble in H_2O,[4] soluble in excess of an alkali iodide, due to the formation of complex ions such as, AgI_2^-. The simple salt is, however, reprecipitated on dilution with H_2O.[5] The tendency of silver halides to form complex anions increases in the order: $AgCl$, $AgBr$, AgI.

Silver iodide is decomposed by concentrated HNO_3 (distinction from $AgCl$ and $AgBr$). It is not appreciably soluble in NH_4OH, especially if the latter is dilute (distinction from $AgCl$), slightly soluble in $Na_2S_2O_3$, less soluble in Na_2SO_3 or NH_4CNS;[6] moderately soluble in KCN,[7] insoluble in $(NH_4)_2CO_3$ (separation from $AgCl$).[8] In the presence of light, AgI is not affected by $FeSO_4$. In water or dilute acids, Zn and Fe give Ag°.[9] Soluble sulfides transpose AgI to Ag_2S.

Bromic acid and soluble bromates precipitate silver bromate, $AgBrO_3$, white, slightly soluble in H_2O,[10] soluble in NH_4OH, forming $Ag(NH_3)_2BrO_3$.

Iodic acid and soluble iodates precipitate silver iodate,[11] $AgIO_3$, white, insoluble in H_2O,[12] slightly soluble in HNO_3, readily soluble in 10% NH_4OH.

g. Soluble arsenites precipitate silver arsenite, Ag_3AsO_3, bright yellow, insoluble in H_2O;[13] readily dissolved by both acids and bases. Soluble

[1] Hoitsema, *Z. physik. Ch.*, **20**, 272 (1896).

[2] By a suitable arrangement of the light, Richards, *Proc. Am. Acad.*, **29**, 74 (1893), was able to detect one part of $AgCl$ in 30 million parts of H_2O.

[3] Hill, *J. Am. Ch. Soc.*, **30**, 68 (1908); Prud'homme, *J. ch. phys.*, **9**, 519 (1911).

[4] Hill, *loc. cit.* The values in the literature are somewhat discordant.

[5] Van Dam and Donk, *Ch. Weekblad*, **8**, 846 (1911).

[6] Valenta, *Monatsh.*, **15**, 249 (1894).

[7] *Idem.*

[8] Baubigny, *Bull. soc. ch.*, **3**, 629 (1908); *Compt. rend.*, **146**, 335 (1908).

[9] Gmelin-Kraut, 7th ed. V, 2, p. 119.

[10] Reedy, *J. Am. Ch. Soc.*, **43**, 1440 (1921).

[11] See Hill and Simmons, *J. Am. Ch. Soc.*, **31**, 827 (1909).

[12] Whitby, *Z. anorg. allgem. Ch.*, **67**, 107 (1910).

[13] *Idem.*

arsenates precipitate silver arsenate,[1] Ag_3AsO_4, brown, insoluble in H_2O, soluble in acids (not acetic), and NH_4OH. Arsine or stibine precipitate silver from aqueous solutions of $AgNO_3$: $AsH_3 + 6\ AgNO_3 + 3\ H_2O = 6\ Ag + H_3AsO_3 + 6\ HNO_3$; $(SbH_3 + 3\ AgNO_3 = Ag_3Sb + 3\ HNO_3)$; $SbH_3 + 6\ AgNO_3 + 3\ H_2O = 6\ Ag + H_3SbO_3 + 6\ HNO_3$.[2]

A solution of alkali stannite, e.g., Na_2SnO_2, precipitates Ag° from solutions of silver salts. A solution of $AgNO_3$ in great excess of NH_4OH gives a very delicate test for tin as Sn^{++} in the presence of a fixed alkali. Antimony does not interfere under the conditions mentioned.

h. Chromates added to an excess of Ag^+ give brownish-red silver chromate, Ag_2CrO_4.[3] The product is insoluble in H_2O, readily soluble in HNO_3, H_2SO_4, or NH_4OH. The solubility in acetic acid depends upon its concentration.[4] Silver dichromate, $Ag_2Cr_2O_7$, bright red, is obtained when a dichromate is added to an acid solution of Ag^+. The salt changes to Ag_2CrO_4 upon boiling with H_2O:[5] $Ag_2Cr_2O_7 + H_2O = Ag_2CrO_4 + H_2CrO_4$. Silver dichromate is insoluble in H_2O,[6] soluble in HNO_3 and NH_4OH.

7. Ignition. — Silver nitrate melts unaltered at 212°; at 320° it commences to decompose: $2\ AgNO_3 = 2\ AgNO_2 + O_2$. As the temperature rises, the reaction becomes more complex, N, O_2 and Ag° being among the products formed.[7] Silver chloride fuses at 451°,[8] AgBr at 419°,[9] AgI at 352°.[10] Mixed with Na_2CO_3 and charcoal, all silver salts are decomposed by heat, giving Ag°. Zinc and other more volatile elements may be separated from Ag by distillation.

8. Detection. — Silver is identified by the successive steps: (1) precipitation as AgCl; (2) digestion with hot water (to remove any $PbCl_2$); (3) solution in ammonium hydroxide (to separate from Hg_2Cl_2); (4) acidification of a portion of the ammoniacal solution with nitric acid which should give a precipitate of AgCl; addition of potassium iodide to a second part of the ammoniacal solution which should produce a pale yellow precipitate of AgI. In order of decreasing solubility, certain of the salts of silver may be arranged as follows: AgCl, AgCN, AgCNS, AgBr, AgI, Ag_2S. Under suitable conditions the formation of any of these compounds may serve as a test for silver.

[1] For the exact preparation and the properties of Ag_3AsO_4, see Baxter and Coffin, *J. Am. Ch. Soc.*, **31**, 297 (1909).
[2] Reckleben, *Ber.*, **42**, 1458 (1909).
[3] See, however, Kohler, *Z. anorg. allgem. Ch.*, **96**, 207 (1916).
[4] Margosches, *Z. anorg. allgem. Ch.*, **51**, 231 (1906).
[5] Autenrieth, *Ber.*, **35**, 2057 (1902).
[6] Mayer, *Ber.*, **36**, 1741 (1903).
[7] Oswald, *Ann. ch.*, [9] **1**, 32 (1914).
[8] Schemtschushny, *J. Russ. Phys. Ch. Soc.*, **48**, 203 (1916); cf. Truthe, *Z. anorg. allgem. Ch.*, **76**, 168 (1912).
[9] Sandonnini, *Atti. accad. Lincei*, [5] **21**, ii, 197 (1912).
[10] Mönkemeyer, *N. Jahrsb. Miner.*, *Beilage*, **22**, 28 (1908).

An aqueous solution of $AgNO_3$, treated with various organic compounds such as dextrine, gum arabic, sugar, or starch, gives, on addition of NaOH, a brown suspension of colloidal silver. The intensity of coloration depends upon the amount of silver present.[1] The test is so delicate that in 50 cc. of solution, one part of Ag in 25 million can be detected. Ammonium hydroxide interferes.

If the silver-ammonia ion is treated with a few cubic centimeters of concentrated NaOH and a few drops of glycerine a grayish precipitate of silver is obtained. The test is very delicate.[2]

Diphenylthiocarbazide gives with Ag^+ a red precipitate that soon turns brown.[3] In a neutral or slightly acid solution, *p*-dimethylaminobenzylidene-rhodanine gives a red precipitate with Ag^+.[4] Kolthoff states that Cu, Hg_2^{++}, and Pb^{++} interfere.[5, 6]

9. Determination. — *Gravimetrically*, silver is usually precipitated as the chloride, dried below 200° and weighed as such. Occasionally electrolytic deposition is employed. *Volumetrically*, titration with standardized NaCl or HCl is the customary procedure, the equivalence point being detected by means of CrO_4^{--}. Thiocyanate may be used as the standard solution, in which case Fe^{+3} is used as the indicator. If an iodide is used as the standard solution, the end point may be ascertained by the formation of dark brown PdI_2 or blue starch iodide. In the latter case, the excess iodide reacts with HNO_2 to liberate the iodine required to color the starch. In either case, the end point is much sharper than with the thiocyanate.

10. Oxidation and Reduction. — Metallic silver precipitates gold and platinum from their solutions, reduces Cu^{++} to Cu_2^{++}, Hg^{++} to Hg_2^{++}, and MnO_4^- to MnO_2. Silver is precipitated from solution by: Pb, PbS, Hg, As, AsH_3, Sb, SbH_3, Sn, Sn^{++}, Bi, Cu, Cu_2^{++}, Cd, Te, Fe, FeS, Al, Mn, Zn, Mg, P, PH_3, H_3PO_2, H_2SO_3, SiH_4, H_2O_2, and H (very slowly).

In alkaline systems silver is also reduced by Hg_2^{++}, As^{+3}, Sb^{+3}, Bi^{+3}, and Mn^{++}. An amalgam of mercury and tin reduces insoluble compounds of silver in the wet way, the silver amalgamates with the mercury, and the tin becomes Sn^{+4}. Ferrous iron incompletely reduces Ag^+ in the cold; on boiling the Fe^{+3} initially formed is reduced and the Ag° dissolved. In the gradual reduction of silver by organic reagents (tartrates, aldehydes, etc.) the metal may be obtained as a bright silver coating, or mirror, upon the inner surface of the test tube or beaker provided the glass surface be scrupulously clean. This reduction apparently does not involve the NO_3^- ion: $4\ AgNO_3 + 2\ H_2O = 4\ Ag + 4\ HNO_3 + O_2$.

[1] This was the basis for the method used by Whitby, *Intern. Cong. Appl. Ch.*, 1909; *C.A.* **4**, 1444, when determining the solubility of various silver salts.

[2] Donath, *Ch. Ztg.*, **32**, 645 (1908).

[3] Parri, *Giorn. farm. ch.*, **73**, 207 (1924).

[4] Feigl, *Z. anal. Ch.*, **74**, 380 (1928).

[5] Kolthoff, *J. Am. Ch. Soc.*, **52**, 2222–6 (1930).

[6] Gutzeit, *Helv. Ch. Acta*, **12**, 713–40 (1929), *C.A.* **23**, 4644, has described some characteristic tests for Ag.

Light acts upon many salts of silver. The halides, particularly AgBr plus a small amount of AgI, are used in the preparation of photographic emulsions. The actinic rays probably decompose some of the salt producing a mixture of the halide with a small quantity of colloidal silver.[1]

[1] Jenckel, *Z. anorg. allgem. Ch.*, **179**, 89 (1929); Kieser, *Z. wiss. Phot.*, **26**, 1, 275 (1928). A summary of modern views on this subject is given by Dhar, "The Chemical Action of Light," Blackie and Sons, Ltd., London, **1931**, Chapter XXVII.

§60. Comparison of Certain Reactions of First-Group (Silver Group) Metals*

	Pb^{++}	Ag^{+}	Hg_2^{++}	Hg^{++}
KOH or **NaOH,** in excess	Solution (§**57**, 6*a*).	**Ag_2O,** grayish brown (§**59**, 6*a*).	**Hg_2O,** black (§**58**, 6*a*).	**HgO**, yellow (§**58**, 6*a*).
NH_4OH, in excess	White precipitate, basic salt, not formed in the acetate (§**57**, 6*a*).	Solution (§**59**, 6*a*).	**Hg** and **NH_2HgNO_3**, black (§**58**, 6*a*).	**NHg_2NO_3** or **NH_2HgCl**, white (§**58**, 6*a*).
Chlorides	**$PbCl_2$**, white, sparingly soluble in cold water, more readily if hot; insoluble in **NH_4OH** (§**57**, 6*f*).	**AgCl**, white, insoluble in water, soluble in **NH_4OH** (§**59**, 6*f*).	**Hg_2Cl_2**, white, insoluble in water, decomposed by **NH_4OH** (§**58**, 6*f*).	....
Bromides	**$PbBr_2$**, less soluble in water than **$PbCl_2$**, insoluble in **NH_4OH** (§**57**, 6*f*).	**AgBr**, yellowish white, soluble in **NH_4OH** (§**59**, 6*f*).	**Hg_2Br_2**, yellowish white, decomposed by **NH_4OH** (§**58**, 6*f*).	**$HgBr_2$**, white, fairly soluble in water, or in the **Hg^{++}** salt or the bromide (§**58**, 6*f*).
Iodides	**PbI_2**, orange yellow, sparingly soluble in the alkali iodides (§**57**, 6*f*).	**AgI**, pale yellow, soluble in the alkali iodides (§**59**, 6*f*).	**Hg_2I_2**, yellowish green, decomposed by the alkali iodides (§**58**, 6*f*).	**HgI_2**, red, readily soluble in the alkali iodides (§**58**, 6*f*).
Sulfates	**$PbSO_4$**, white, almost insoluble in water (§**57**, 6*e*).	**Ag_2SO_4**, white, if solution be not too dilute (§**59**, 5*c*).	**Hg_2SO_4**, white, if solution be not too dilute (§**58**, 5*c*).	....
Chromates	**$PbCrO_4$**, yellow, soluble in **KOH** (§**57**, 6*h*).	**Ag_2CrO_4**, purple red, soluble in **NH_4OH** (§**59**, 6*h*).	**Hg_2CrO_4**, orange yellow (§**58**, 6*h*).	Basic salt, yellow to reddish yellow (§**58**, 6*h*).
Zinc	**Pb** (§**57**, 10).	**Ag** (§**59**, 10).	**Hg** (§**58**, 10).	**Hg_2^{++}** and then **Hg** (§**58**, 10).
Lead	....	**Ag** (§**59**, 10).	**Hg** (§**58**, 10).	**Hg_2^{++}** and then **Hg** (§**57**, 10).
Mercury	....	**Ag** (§**59**, 10).	....	....
Stannous Salts	....	**Ag** (§**59**, 6*g*).	**Hg** (§**58**, 6*g*).	**Hg_2^{++}** and then **Hg** (§**58**, 6*g*).

* Neutral or slightly acid solutions of the nitrates may be used.

§61. Outline for the Analysis of the First Group (Silver Group).

METALS WHOSE NORMAL CHLORIDES ARE INSOLUBLE
($PbCl_2$ IS SLIGHTLY SOLUBLE)

Metals	Ag	Hg	Pb
Ions in acid solution	Ag^+	Hg_2^{++}	Pb^{++}
Ions in NaOH solution	——	——	PbO_2^{--}
Ions in NH_4OH solution	$Ag(NH_3)_2^+$	——	——

<table>
<tr><td colspan="3">If original soln. is alkaline, acidify with HNO_3</td></tr>
<tr><td>Ag^+</td><td>Hg_2^{++}</td><td>Pb^{++}</td></tr>
<tr><td colspan="3">HCl (slight excess)</td></tr>
<tr><td>$AgCl$</td><td>Hg_2Cl_2</td><td>$PbCl_2$</td></tr>
<tr><td colspan="3">Hot H_2O</td></tr>
<tr><td>$AgCl$</td><td>Hg_2Cl_2</td><td rowspan="3">$PbCl_2$
1. $H_2SO_4 \rightarrow PbSO_4$
2. $KI \rightarrow PbI_2$
3. $K_2Cr_2O_7 \rightarrow PbCrO_4$</td></tr>
<tr><td colspan="2">NH_4OH</td></tr>
<tr><td>$Ag(NH_3)_2Cl$
1. $HNO_3 \rightarrow AgCl$
2. $KI \rightarrow AgI$</td><td>$NH_2HgCl + Hg$</td></tr>
</table>

DIRECTIONS FOR THE PRECIPITATION AND ANALYSIS OF THE FIRST GROUP

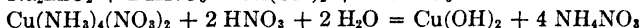
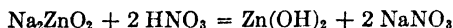
§62. **Manipulation.** — To the cold solution, slightly acid with HNO_3, add HCl (whenever directions call for the addition of a reagent it is to be used reagent strength unless otherwise stated) 6–8 drops at a time, shaking thoroughly after each addition, until no further precipitate forms. The precipitate will consist of chlorides of Pb, Hg^I and Ag. Shake thoroughly and allow to stand a few moments before filtering. Pour the solution and precipitate onto a filter paper previously wetted with dilute HCl, and wash 2–3 times with cold water, or until the filtrate is only faintly acid to

litmus. The first washings should be added to the main filtrate, which is marked and set aside to be tested for the metals of the remaining groups. (§80.)

§63. Notes. — 1. If the original solution is alkaline it must first be acidified before precipitating Group I, since AgCl and $PbCl_2$ do not precipitate readily in alkaline solution.

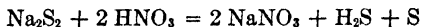
2. Nitric acid is used rather than HCl to acidify the original solution for 2 reasons: (1) to avoid adding so much Cl^- that the Group I metals might be converted to complex chlorides ($AgCl_3^{--}$, $PbCl_4^{--}$) and thus fail to precipitate; (2) to avoid confusing Group I chlorides with other precipitates that might form from other materials present in the solution. Some of the more important cases of this latter sort are as follows:

a. Alkaline solutions of the amphoteric hydroxides and certain of the ammonia complexes (in the absence of high concentration of NH_4^+) may precipitate when neutralized with acids.

$$Na_2ZnO_2 + 2\,HNO_3 = Zn(OH)_2 + 2\,NaNO_3$$
$$Cu(NH_3)_4(NO_3)_2 + 2\,HNO_3 + 2\,H_2O = Cu(OH)_2 + 4\,NH_4NO_3$$

b. The thio salts of As, Sb, Sn (Au, Pt, Mo, Ir, W, Be, V, Se and Te), in solutions of alkali sulfides precipitate as sulfides on the addition of acid.

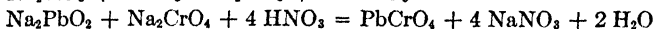
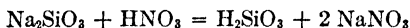
$$2\,Na_3AsS_4 + 6\,HCl = As_2S_5 + 6\,NaCl + 3\,H_2S$$

c. Soluble polysulfides and thiosulfates form a precipitate of S(white) on the addition of acid.

$$Na_2S_2 + 2\,HNO_3 = 2\,NaNO_3 + H_2S + S$$

d. Certain less stable complex cyanides, as $K_2Ni(CN)_4$, are changed to insoluble cyanides, $Ni(CN)_2$, on the addition of acid.

$$K_2Ni(CN)_4 + 2\,HNO_3 = 2\,KNO_3 + Ni(CN)_2 + 2\,HCN$$

e. Solutions of silicates (§249, 6), borates, tungstates, molybdates; certain combinations of metals with chromates and thiocyanates; also benzoates, salicylates, urates and certain other organic salts, are precipitated by acids.

$$Na_2SiO_3 + HNO_3 = H_2SiO_3 + 2\,NaNO_3$$
$$Na_2PbO_2 + Na_2CrO_4 + 4\,HNO_3 = PbCrO_4 + 4\,NaNO_3 + 2\,H_2O$$

f. Acidification may induce changes of oxidation or reduction which in some cases may result in precipitation: for example, Na_2MnO_4 (§134, 4, *e*), mixtures of Na_2S and Na_2SO_3 (§265, 6B, 4), KI and KIO_3 (§280, 6B, 7) etc.

$$3\,Na_2MnO_4 + 4\,HNO_3 = MnO_2 + 2\,NaMnO_4 + 4\,NaNO_3 + 2\,H_2O$$

Many of the above precipitates dissolve on further addition of acid. If the precipitate, obtained on addition of nitric acid to the solution, does not dissolve readily in excess, it should be separated by filtration, and treated as a solid substance taken for examination (see §301).

3. Hydrochloric acid, added to certain neutral or slightly acid solutions, may cause a precipitate to form even when none of the Group I metals are present:

(a) Concentrated solutions of certain chlorides ($BaCl_2$ and NaCl) may form precipitates, readily soluble on diluting with water (§186, 5, *c*, §206, 6, *f*).

(b) Certain solutions of Sb, Bi and Sn, not containing free HCl, precipitate as oxychloride on addition of this acid (§70, 6, *b*, §76, 6, *f*). These precipitates dissolve fairly readily in excess of the HCl.

4. Failure to obtain a precipitate upon the addition of HCl is usually proof of the absence of Hg^{I} and Ag; but $PbCl_2$ will not precipitate unless the concentration of Pb^{++} is relatively high. However, small amounts of Group I may not precipitate if the solution contains high concentration of either Hg^{++} (§58, 5, *c*; §59, 5, *c*), or Cl^- (§58, 6, *c*; §59, 6, *c*). In such cases the Group I metals will be found in Group II.

5. The presence of slight excess of dilute HCl does not affect appreciably the completeness of precipitation of Hg_2Cl_2 and AgCl (since these are relatively insoluble in H_2O), but, as $PbCl_2$ is moderately soluble in H_2O and only slightly soluble in dilute HCl, an excess of the reagent is necessary to secure maximum precipitation of Pb in Group I.

6. The use of large excess of HCl should be avoided, because secondary reactions may take place causing some redissolving of the precipitates with formation of complex ions ($AgCl_3^{--}$, $PbCl_4^{--}$, $Hg_2Cl_4^{--}$).

7. The solution must be cold when precipitating Group I because $PbCl_2$ is readily soluble in warm or hot solution.

8. Many precipitates form slowly when the solution is rather dilute. This is especially true of $PbCl_2$ in Group I. Therefore it is desirable to let the solution stand a short time after adding HCl in order that $PbCl_2$ may form if no precipitate is obtained immediately, or may precipitate more completely.

9. Each group should be precipitated as completely as possible so as to avoid interferences in later groups. After the Group I precipitate has been filtered out the filtrate should be treated with a few drops of HCl. If further precipitate forms, precipitation was incomplete. In that case add more HCl, shake, let stand a short time, filter, and test filtrate again.

§64. **Manipulation.** — Transfer the white precipitate (§62) to a beaker, add 15–20 cc. H_2O, digest at the boiling point for 1–2 minutes, and filter promptly. Lead chloride dissolves fairly readily in hot water. Wash the residue once or twice with hot water, discarding the washings, then set aside to test for Ag and Hg (§66).

Divide the filtrate into 3 portions and test separately for lead with the following reagents: (1) H_2SO_4, (2) KI, (3) $K_2Cr_2O_7$ (§57, 6, *e*, *f*, *h*).

$$PbCl_2 + H_2SO_4 = PbSO_4 \text{ (white)} + 2\,HCl$$

$$PbCl_2 + 2\,KI = PbI_2 \text{ (yellow)} + 2\,KCl$$

$$2\,PbCl_2 + K_2Cr_2O_7 + H_2O = 2\,PbCrO_4 \text{ (yellow)} + 2\,KCl + 2\,HCl$$

§65. **Notes.** — 1. Lead is never completely precipitated in Group I (§57, 6, *f*). The presence of moderate excess of dilute HCl and the cooling of the solution both favor the precipitation.

2. Instead of transferring the precipitate to a beaker and digesting with hot water, it is possible to extract the $PbCl_2$ from the precipitate on the filter by pouring 15–20 cc. of hot water through the filter, catching the filtrate in a clean test tube, heating and pouring it through the filter again. This type of procedure does not permit as long contact of the reagent with the precipitate as the one recommended above, and so can be used only in cases where the precipitate reacts fairly rapidly with the reagent.

3. If the $PbCl_2$ is not all washed out with hot water it is changed to an insoluble basic salt (white) by the NH_4OH used later to separate Ag from Hg. However, this precipitate can be removed by filtering, so it does not interfere with the later tests.

4. Lead sulfate is an unusually compact precipitate that forms slowly in dilute solution. Care should be taken not to overlook this precipitate when testing for small amounts of lead.

5. Lead iodide is appreciably soluble in warm or hot solution, so precipitation may not take place immediately on adding the KI. In such a case cooling will cause the formation of beautiful golden-yellow crystals of PbI_2. If the original precipitate of PbI_2 is flocculent it may be converted to the crystalline form by dissolving in hot water and cooling slowly (characteristic of lead).

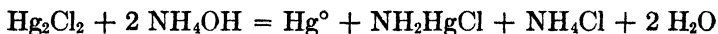
6. A slight excess of KI should be used to dissolve any possible HgI_2 (occasionally obtained, due to incomplete washing of the Group I precipitate), but large excess is to be avoided since PbI_2 is slightly soluble therein.

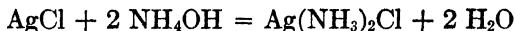
7. The chromate test is the most dependable of the three, $PbCrO_4$ forming readily as a bulky, yellow precipitate (soluble in NaOH as distinction from Ba and Bi, §76, 6, *h*; §186, 6, *h*), whether the solution is hot or cold.

8. Hydrosulfic acid is sometimes used to detect Pb. The test is not characteristic, for many of the metals form black precipitates with this reagent, but it is very delicate, a brown color appearing in solutions as dilute as 1 : 1,000,000.

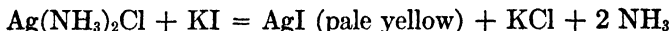
9. Lead may exist in the original solution chiefly as lead ion (Pb^{++}) or plumbite ion (PbO_2^{--}). Since $Pb(OH)_2$ is insoluble in water and requires excess of acid to convert it to Pb^{++}, or excess of alkali to convert it to PbO_2^{--}, the former will be found in acid solution and the latter in alkaline solution.

§66. Manipulation. — Transfer the white precipitate (§64) to a beaker, add 5 cc. of diluted NH_4OH (1 volume of reagent plus 1 volume of water), warm slightly, let stand a minute or two, then filter and wash. If mercurous mercury is present the white precipitate blackens instantly as the NH_4OH is added.

$$Hg_2Cl_2 + 2\ NH_4OH = Hg^\circ + NH_2HgCl + NH_4Cl + 2\ H_2O$$

The AgCl is dissolved by the NH_4OH,

$$AgCl + 2\ NH_4OH = Ag(NH_3)_2Cl + 2\ H_2O$$

and is found in the filtrate. If the ammoniacal filtrate is cloudy, pour it through the filter again. Divide the solution into two parts. To one add a few drops of KI, to the other add HNO_3 until acid (shake solution and test with litmus).

$$Ag(NH_3)_2Cl + KI = AgI \text{ (pale yellow)} + KCl + 2\ NH_3$$

$$Ag(NH_3)_2Cl + 2\ HNO_3 = AgCl \text{ (curdy, white)} + 2\ NH_4NO_3$$

§67. Notes. — Mercury. — 1. The black precipitate on the filter, caused by the addition of NH_4OH to the Hg_2Cl_2, may be examined under the microscope for globules of Hg°, or the precipitate may be digested with a concentrated solution of $(NH_4)_2SO_4$, which dissolves the NH_2HgCl, leaving the Hg° (§58, 6, *a*).

2. If the original solution contains no interfering metals, the distinctive reactions of mercurous salts with iodides, chromates and phosphates may be obtained (§58, 6, *e*, *h*, *d*).

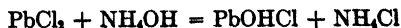
3. The precipitation with HCl followed by blackening with NH_4OH is conclusive evidence of the presence of Hg^I; should further confirmation of Hg be desired, the black precipitate may be dissolved in nitrohydrochloric acid (or sodium hypochlorite), the excess acid removed by evaporation, and the resulting solution tested for $HgCl_2$ with $SnCl_2$ or metallic Cu (§58, 10).

4. Mercury has but few soluble mercurous compounds, and in preparing solutions of the insoluble compounds for analysis oxidizing agents are usually employed and the Hg is found only in Group II (§96, §97).

5. Mercurous mercury is found in solution commonly only in the one form, Hg_2^{++}.

§68. Silver. — 1. Silver chloride may be extracted from the precipitate by repeated treatment on the filter with a small amount of NH_4OH. The separation is less complete, however, the rate of dissolving of AgCl in NH_4OH being slowed up appreciably by the earlier digesting of AgCl in the hot solution.

2. A white precipitate appearing in the ammoniacal filtrate may be due to $PbCl_2$ not completely washed out with the hot water.

$$PbCl_2 + NH_4OH = PbOHCl + NH_4Cl$$

It should not be mistaken for AgCl but should be filtered out and discarded before the test for Ag is applied.

3. With a large amount of Hg_2Cl_2 present the AgCl does not dissolve completely, due to reduction by Hg° (formed by action of NH_4OH on Hg_2Cl_2) to Ag° which is insoluble in NH_4OH.

4. If Hg^I is present and Ag not detected, the black precipitate should be digested for several minutes with hot nitrohydrochloric acid (or NaClO), the excess acid removed by evaporation, and the solution diluted to 15–20 cc. with water. The Hg will be converted to $HgCl_2$ (soluble), while AgCl remains undissolved. The latter should be filtered out, washed, dissolved in NH_4OH, and identified in the usual way (§66). This procedure may also be used instead of NH_4OH for treatment of the Hg_2Cl_2–AgCl mixture after removal of the $PbCl_2$.

5. An interesting test for Ag may be made on the original solution, depending on the fact that Mn may be oxidized to $HMnO_4$ (reddish purple) by $K_2S_2O_8$ if Ag is present, but not if it is absent. To a slightly acid portion of the original solution add 0.3–0.5 g. of $K_2S_2O_8$. Boil to oxidize other reducing agents, then add 1 drop of a dilute $MnSO_4$ solution, a little more $K_2S_2O_8$, and boil again.

6. Silver is usually present in the original solution either as silver ion (Ag^+) or silver-ammonia ion ($Ag(NH_3)_2^+$). The former exists in neutral or acid solution, while the latter is found only in an ammoniacal solution.

7. If only one metal of the first group is present, the action of NH_4OH on the Group I precipitate would determine which it is: $PbCl_2$ does not change color or dissolve; Hg_2Cl_2 turns black; AgCl dissolves (§60).

§68A. Thallium (L. *thallus* = a budding twig). Tl = 204.39. Atomic No. 81. Valence 1 and 3. Discovered by Crookes in 1861.

1. Physical Properties. — Density, 11.85 at 20°;[1] melting point, 303.5°;[2] boiling point, 1462° at 760 mm. pressure.[3] Tl commences to volatilize at about 174°, it may be distilled in an atmosphere of hydrogen. Metallic thallium is silvery-white with a distinctly blue-gray tinge when a freshly exposed surface is observed. After a short time the color changes to dark gray. Oxidation of the metal, other than this superficial change, is very slow at 25° but increases with temperature. Thallium is softer than Pb, easily cut with a knife, malleable and of low tenacity. It can be extruded but not drawn into wire. It is crystalline in structure, existing in two modifications. The transition temperature is 226°. Tl is a poor conductor of electricity. In the electromotive series it lies between Fe and Co. The various compounds of Tl are poisonous, hence its use as an insecticide and rat poison.[4] It is also used in making optical glass, in the "Thalofide" cell,[5] in medicine, and as an anti-knock compound in gasoline.[6] Thallium alloys readily with many metals, e.g., Hg, Mg, Ca, Ag, Cd, Cu and Zn. An alloy consisting of 10% Tl, 20% Sn and 70% Pb resists the action of H_2SO_4, HNO_3 and HCl.[7]

[1] Richards and Wilson, *Z. physik. Ch.*, **72**, 141 (1910).
[2] Richards and Smyth, *J. Am. Ch. Soc.*, **44**, 524 (1921).
[3] Mellor, V, 412. Cf. Hopkins, p. 124, who gives 1515°.
[4] Popenoe, *Science*, **64**, 525 (1926); Enck, *Foote-Prints*, **2**, No. 1, 15–7 (1929).
[5] *Phys. Rev.* [2] **15**, 289 (1920). U. S. Patent 1,301,227.
[6] British Patent 279,560.
[7] Cf. British Patent 297,665.

2. Occurrence. — Swedish crooksite, $(CuTlAg)_2Se$, contains 16%–19% Tl; lorandite, $TlAsS_2$, from Macedonia, contains 59.5% Tl; hutchinsonite, a complex sulfide, carries 18%–25% Tl; vrbaite, $TlAs_2Sb_5$, is 29%–32% Tl. Small amounts of the element are also found in pyrites, zinc blende, hematite, etc. Commercially, thallium is of minor importance. It is usually sold as the sulfate, Tl_2SO_4, or metal. Early in 1931 the price of this latter form was $12–$15 a pound.

3. Preparation. — The commercial supply of thallium was formerly obtained from the flue dust of sulfuric acid plants using pyrites as a raw material. At present the major amount is produced as a by-product of cadmium refining. To obtain Tl from one of its minerals, a satisfactory general method is to treat the finely powdered sample with K_2SO_4 and H_2SO_4 and heat to complete decomposition. After dilution, filtration and neutralization with Na_2CO_3, any Pb or Bi is precipitated by means of NaCN. The filtrate, treated with $(NH_4)_2S$, gives a precipitate of the sulfides of Tl, Cd, etc. The Tl_2S is separated by dissolving it in dilute H_2SO_4, which does not appreciably affect the other sulfides. Metallic Tl may be obtained from the sulfate solution by electrolysis.[1]

A general method for the recovery of thallium from flue dust is to boil the sample with water, let stand over night, filter and add HCl to the filtrate. The crude TlCl that separates may be converted to the sulfate, and after removal of impurities, again precipitated as the chloride. The precipitate may be dried and fused with Na_2CO_3 and NaCN to obtain Tl°.

4. Oxides and Hydroxides. — Thallium forms two[2] well defined oxides: thallous, Tl_2O, and thallic, Tl_2O_3. Two hydroxides (or hydrated oxides) also have been obtained: thallous, TlOH (or $Tl_2O \cdot H_2O$), and thallic, TlOOH (see below). Thallous oxide, black, is obtained when TlOH is heated above 100° or when Tl is heated above a bright red. The product is fusible and in the molten state attacks glass or porcelain. It readily absorbs H_2O, forming yellow TlOH, which in turn will dissolve if sufficient water is present. Thallous hydroxide is about as strong a base as sodium hydroxide. It rapidly absorbs CO_2 from the air and is readily oxidized by Cl_2, H_2O_2, etc. Paper soaked in TlOH solution has been suggested for the detection of ozone, since a very small amount of that gas will turn the paper brown. Thallic oxide, dark brown to black, is obtained (1) by heating Tl° to a dull red,[3] (2) by electrolysis of thallous sulfate or nitrate, using platinum electrodes and a potential of 1.43 volts. Thallic oxide is feebly basic, insoluble in H_2O or the alkalis, and is but slightly affected when boiled with water. When the solution of a thallic salt is treated with a base, a brown precipitate is obtained that is very insoluble and does not possess acidic properties. Some investigators believe this product to be $Tl(OH)_3$, but it apparently has not been isolated as such. On heating or drying, the compound resulting is metathallic hydroxide, TlOOH (or $Tl_2O_3 \cdot H_2O$).

5. Solubility. — *a. Metal.* — The best solvent for Tl° is HNO_3 which forms chiefly Tl^+ with possibly a small amount of Tl^{+3}; solution is slow in HCl; aqua regia gives Tl^{+3}; with H_2SO_3, action is slow and Tl_2SO_3 is formed, while with H_2SO_4, dilute, a slow formation of Tl_2SO_4 takes place; with the concentrated acid, solution is readily effected. If metallic thallium is placed under water, then agitated with air, the metal will dissolve to form TlOH.

b. Oxides and Hydroxides. — Thallous oxide is readily soluble in H_2O to form thallous hydroxide, which dissolves to the extent of 343.4 g. per liter at 18.5°.[4] Thallic oxide is insoluble in H_2O, slightly soluble in cold H_2SO_4. The warm acid causes decomposition to Tl^+ and O_2. Cold HCl readily forms Tl^{+3}. Metathallic hydroxide is only slightly soluble in H_2O, insoluble in the fixed alkalis, readily soluble in the common acids when freshly precipitated, but after drying reacts with HCl to form Cl_2 and with H_2SO_4 to give O_2. Its solubility product at 25° is said to be $10^{-53.5}$

c. Salts. — The lower valence of thallium resembles the fixed alkalis, in that its hydroxide, carbonate and sulfate are soluble while the chloroplatinate and cobaltinitrite are insoluble. It also resembles Pb in that its sulfide and chromate are insoluble and its

[1] Cf. Brown and McGlynn, *Trans. Am. Electroch. Soc.*, **53**, 351 (1928); Richards and Smyth, *J. Am. Ch. Soc.*, **44**, 524 (1922).

[2] Others have been reported, but will not be considered here.

[3] Decomposition to Tl_2O starts at about 800°, is rapid at 1000°.

[4] Cf. Friend, IV, 185.

[5] Abegg and Spencer, *Z. anorg. allgem. Ch.*, **44**, 379 (1905).

halides are insoluble in cold water, moderately soluble in hot water. Of the salts not covered by the above generalization, the acetate, nitrite, nitrate, chlorate, perchlorate and ferricyanide are soluble; the sulfite, thiocyanate and oxalate are moderately soluble; the phosphate (Tl_3PO_4) and arsenite are slightly soluble. Thallous sulfide is practically insoluble in NH_4OH, KCN, $(NH_4)_2S$, NaOH and Na_2CO_3; it is slightly soluble in HCl and acetic acid, readily soluble in HNO_3. The thallic halides, nitrate and sulfate are soluble in water but tend to hydrolyze more readily than the corresponding thallous salts.

6. Reactions. — *a.* A dilute solution of Tl^+ gives no precipitate with NaOH, NH_4OH or Na_2CO_3. The thallic ion, with these reagents, partially precipitates as brown thallic hydroxide. (See 4 above.) The precipitate is insoluble in excess reagent.

b. Thallous ion reacts with KCNS to give a white crystalline precipitate of TlCNS.

d. Sodium phosphate does not precipitate thallium from neutral or acid solution, but from alkaline solution a crystalline, white precipitate quickly separates.

e. Hydrosulfic acid does not precipitate thallium from strongly acid solution, but separations from other ions based on this fact are of little value because the thallium is carried down with the sulfide formed. In acetic acid, neutral, or alkaline solution Tl^+ may be completely precipitated as Tl_2S. The precipitate is rapidly oxidized to Tl_2SO_4 on exposure to the air.[1] Thallic sulfide is not obtained when Tl^{+3}, in either acid or alkaline solution, is treated with a sulfide, the Tl^{+3} is reduced to Tl^+ and sulfur is liberated. If Tl^+ is treated with $Na_2S_2O_3$, a white precipitate is formed. It is not affected by NH_4OH, but addition of an acid is said to produce Tl_2S. Thallous sulfate forms a series of alums corresponding to the alkali sulfates.

f. Tl^+, treated with a soluble chloride, forms thallous chloride, TlCl, white, somewhat curdy, becoming compact on standing. The product is soluble in hot water, from which, on cooling, a crystalline precipitate separates. Thallic salts do not react with HCl except possibly to form more complex compounds. Thallic chloride when heated gives TlCl and Cl_2. The reaction is reversible, which makes possible a separation from Ag^+. Hypochlorites oxidize Tl^+ to Tl^{+3} in the cold. The chemical reactions of the bromides and iodides resemble those of the chloride. Thallous iodide, when freshly precipitated, is yellow, but on standing becomes distinctly green; it is also only slightly soluble in $Na_2S_2O_3$ (distinction from PbI_2). There is apparently some question as to whether the product obtained by the interaction of Tl^{+3} and an iodide is TlI_3 or $TlI \cdot I_2$. Soluble iodates give, with Tl^+, a white precipitate of thallous iodate, $TlIO_3$.[2]

g. Thallous salts give, with soluble chromates, a yellow precipitate of thallous chromate, Tl_2CrO_4, soluble in cold HNO_3 or H_2SO_4; with Tl^{+3} there is no reaction. Tl^+ reacts with H_2PtCl_6 to give a pale orange precipitate of thallous chloroplatinate, Tl_2PtCl_6;[3] with sodium cobaltinitrite a light red precipitate of thallous cobaltinitrite, $Tl_3Co(NO_2)_6$ is obtained.[4]

7. Ignition. — Thallium imparts a green color to the Bunsen burner flame. Viewed with the spectroscope, a prominent line is observed at 535 $m\mu$.

8. Detection. — Thallium is probably best detected spectroscopically, as little as 0.0002% being discernible. In the wet way, Tl^+ may be precipitated as the chloride in Group I, separated from AgCl and Hg_2Cl_2 by solution in hot H_2O and from $PbCl_2$ by means of H_2SO_4. In the absence of Group II ions, thallium may be precipitated as the sulfide from the neutral or alkaline solution and, ultimately, separated from the other Group III and IV metals.[5] Confirmatory tests for Tl involve the formation of yellow Tl_2CrO_4, yellow Tl_2PtCl_6, red $Tl_3Co(NO_2)_6$, etc. A small amount of Tl^{+3} can readily be detected in the presence of Tl^+ by the formation of a blue color with α-naphthol or benzidine acetate.

9. Determination. — *Gravimetrically,* thallium may be precipitated and weighed as Tl_2CrO_4, Tl_2PtCl_6 or TlI. In the latter case, results are usually low, due to the slight

[1] Pélabon, *Compt. rend.*, **173**, 142 (1921), has studied the properties of Tl_2S.

[2] For a more extensive consideration of the halogen compounds of thallium, see: Thomas, *Ann. ch. phys.*, [8] **11**, 204 (1907); Stortenbeker, *Rec. trav. ch.*, **26**, 248 (1907).

[3] Neumann, *Ann.*, **244**, 349 (1888).

[4] Tanatar and Petrov, *J. Russ. Phys. Ch. Soc.*, **42**, 94 (1911); *C.A.* **5**, 1036.

[5] Noyes, Bray and Spear, *J. Am. Ch. Soc.*, **30**, 481 (1908).

solubility of the halide. *Volumetrically,* direct titration of Tl^+ with KIO_3[1] and with $KMnO_4$[2] have been suggested.[3]

10. Oxidation and Reduction. — Metallic thallium is oxidized to Tl^+ by atmospheric oxygen in the presence of water. Tl^+ is oxidized to Tl^{+3} by strong oxidizing agents: $KMnO_4$, PbO_2, Na_2O_2, NaClO, Cl_2 and aqua regia (but not by HNO_3 alone). Tl^{+3} is reduced to Tl^+ by $SnCl_2$, H_2SO_3, hot H_2O, $FeSO_4$, AsO_3^{-3}, H_2S, NH_2OH, etc. Metallic Zn, Mg, or Al will reduce thallium ions to Tl°.

THE ARSENIC AND COPPER GROUP (SECOND GROUP)

ARSENIC, ANTIMONY, TIN, GOLD, PLATINUM, MOLYBDENUM, **MERCURY, LEAD, BISMUTH, COPPER, CADMIUM** (RUTHENIUM, RHODIUM, PALLADIUM, IRIDIUM, OSMIUM, TUNGSTEN, RHENIUM, GERMANIUM, SELENIUM, TELLURIUM).

THE ARSENIC GROUP (SECOND GROUP, DIVISION A)

ARSENIC, ANTIMONY, TIN, GOLD, PLATINUM, MOLYBDENUM, IRIDIUM, TUNGSTEN, GERMANIUM, SELENIUM, TELLURIUM.

§69. **Arsenic** [Gr. *arsenikos* = male, or Persian *zirne* (zar = gold)] **As** = 74.96. Atomic No. 33. Valence 3 and 5. Discovered by Schroder in 1694.

1. Physical Properties. — Density, metal, 5.7;[4] yellow, 2.0;[5] amorphous, 3.693 at 15°/15°;[6] melting point 817–18° at 35.8 atmospheres;[7] sublimes at 616° under 760 mm.;[8] boiling point 610° at 760 mm. (calc.).[9] Arsenic exists in four allotropic forms, metallic, yellow, gray and brown. Metallic arsenic is steel gray with a metallic luster, brittle and easily pulverizable. It forms beautiful, rhombic crystals on sublimation with slow condensation. The vapor of arsenic is colorless[10] with an oppressive odor.

[1] Berry, *Analyst*, **51**, 137–9 (1926).

[2] Berry, *J. Ch. Soc.*, **121**, 394 (1922). For other procedures, see Strecker and Peña, *Z. anal. Ch.*, **67**, 256 (1925–6).

[3] For the separation of Tl from tervalent and quadrivalent metals, see: Moser and Reif, *Monatsh.*, **52**, 343 (1929).

[4] I. C. T.

[5] Erdmann and Reppert, *Ann.*, **361**, 12 (1908).

[6] Laschtschenko, *J. Ch. Soc.*, **121**, 972 (1922).

[7] Horiba, *Z. physik. Ch.*, **106**, 295 (1923).

[8] Jonker, *Z. anorg. allgem. Ch.*, **62**, 103 (1909); Ruff and Mugdan, *Ibid.*, **117**, 153 (1921), give 633°.

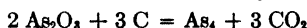
[9] Johnston, *Ind. Eng. Ch.*, **9**, 873 (1917).

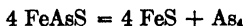
[10] *Schuller, Chem. Ztg.*, **12**, 271 (1888).

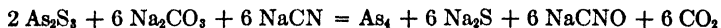
It is slowly oxidized in moist air at ordinary temperatures. When heated in the air As burns with a bluish flame and becomes white arsenious oxide, As_2O_3. The burning metal evolves a strong, garlic-like odor not noticed when pure As_2O_3 is sublimed. In its physical properties arsenic is a metal, but its failure to act as a base with oxygen acids classes it chemically with the non-metals. Its chief use as a metal is in mixing with lead for making shot, though most of the arsenic consumed in the United States is used in insecticides or wood preservatives.

2. Occurrence. — Arsenic is very widely distributed geographically. Arsenopyrite, (mispickel), FeAsS, is the most important mineral. Realgar, AsS,[1] and orpiment, As_2S_3, are used as pigments in paints. Most sulfide ores of zinc and iron contain arsenic, hence it is usually found in these metals as well as in sulfuric acid made from sulfur. The United States (Montana and Utah) is easily the world's largest producer and consumer of arsenic. Measured in terms of white arsenic, As_2O_3, the production in 1928 was 11,767 tons, over 90% of which was from copper ores and the remainder from lead and gold ores. Imports during the same year were 11,153 tons, chiefly from Mexico, Canada, Europe and Japan. The price in 1928 was about 4 cents per pound.

3. Preparation. — (1) Reduction from the oxide by distillation with carbon:

$$2\,As_2O_3 + 3\,C = As_4 + 3\,CO_2$$

(2) from arsenopyrite by ignition in the absence of air:

$$4\,FeAsS = 4\,FeS + As_4$$

(3) from orpiment by fusion:

$$2\,As_2S_3 + 6\,Na_2CO_3 + 6\,NaCN = As_4 + 6\,Na_2S + 6\,NaCNO + 6\,CO_2$$

4. Oxides. — Arsenic forms two oxides: arsenious oxide or anhydride, As_2O_3, more likely As_4O_6,[2] and arsenic oxide or anhydride, As_2O_5. Arsenious oxide, As_2O_3 (white arsenic, arsenious anhydride, arsenious acid, arsenic trioxide), is formed when the metal or the sulfide is heated in air. It sublimes easily on gradually heating, forming beautiful octahedral and tetrahedral crystals. Heated rapidly under pressure it melts and, on cooling, forms the opaque arsenic glass. It is very poisonous.[3] No acids (hydroxides) of As_2O_3 have been isolated; its solutions with bases form salts, arsenites, as if derived from meta-, ortho-, or pyroarsenious acid. The alkali arsenites are usually meta-compounds; the alkaline earth and heavy metal arsenites are usually ortho-compounds.[4] Arsenic oxide, As_2O_5 (arsenic anhydride, arsenic pentoxide), is formed by heating arsenic acid, H_3AsO_4, or by the oxidation of As_2O_3 suspended in HNO_3 (conc.): $As_2O_3 + O_2 = As_2O_5$.[5] It is a white, amorphous mass, melts at a dull red heat; is slowly deliquescent, combining with H_2O to form H_3AsO_4. The pentoxide forms three acids: $As_2O_5 \cdot H_2O$ or $HAsO_3$, meta-arsenic acid; $As_2O_5 \cdot 2H_2O$ or $H_4As_2O_7$, pyroarsenic acid; $As_2O_5 \cdot 3H_2O$ or H_3AsO_4, orthoarsenic acid.[6] Each of these forms a distinct class of arsenates with bases.

5. Solubilities. — *a. Metal.* — Arsenic is insoluble in pure water. It is readily attacked by dry fluorine, chlorine and bromine upon contact and by iodine with the aid of heat. The corresponding arsenious halide is formed. Chlorine and bromine in the presence of water oxidize it first to arsenious then to arsenic acid: $As_4 + 10\,Cl_2 + 16\,H_2O = 4\,H_3AsO_4 + 20\,HCl$. It combines with sulfur forming As_2S_2 to As_2S_5, depending upon the proportion of sulfur present. It is not attacked by concentrated hydrochloric acid at ordinary temperatures, slowly attacked by the hot acid in presence of air forming As_2O_3, then $AsCl_3$; HNO_3 readily oxidizes it to As_2O_3 and H_3AsO_4; upon fusion with an alkali nitrate it becomes arsenate. It dissolves readily in nitrohydrochloric acid forming H_3AsO_4; H_2SO_4, dilute and cold, is without action; with heat and

[1] Sometimes written As_2S_2.

[2] Bozorth, *J. Am. Ch. Soc.*, **45**, 1621 (1923).

[3] Mellor, IX, 42–7.

[4] For various properties of an aqueous solution of As_2O_3, see Anderson and Story, *J. Am. Ch. Soc.*, **45**, 1102–5 (1923).

[5] Zieler, *Z. anorg. allgem. Ch.*, **162**, 161 (1927).

[6] Mellor, IX, 140.

concentrated acid As_2O_3 and SO_2 are formed.[1] NH_4OH is without action. The hot solution of an alkali hydroxide dissolves it, forming the corresponding arsenite and some arsine.[2]

b. Oxides. — Arsenious oxide exists in two forms, crystalline and amorphous, the solubilities of which differ considerably. At ordinary temperatures 100 parts of water dissolve 3.7 parts of the amorphous and 1.7 parts of the crystalline; in boiling water the solubility is three to five times greater.[3] The presence of acids greatly increases the solubility. As_2O_3 is readily soluble in alkali hydroxides or carbonates,[4] forming arsenites. Arsenic pentoxide, As_2O_5, is deliquescent and soluble in water forming H_3AsO_4. The meta- and pyro-acids are easily soluble in water forming the ortho-acid. A solution of $As_2O_5 \cdot 4H_2O$ will contain, at 20°, 86.3% of the tetrahydrate.[5]

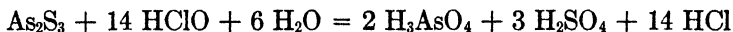
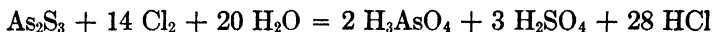
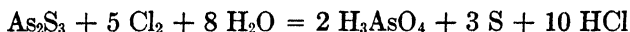
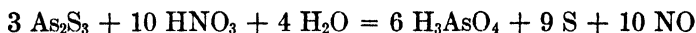
c. Salts. — Arsenic does not act as a base with oxygen acids, but its oxides combine with the metallic oxides to form two classes of salts, arsenites and arsenates. Arsenites of the alkalis are soluble in water, all others are insoluble or slightly soluble; all are easily dissolved in acids. Alkali arsenates, and acid arsenates of the alkaline earths, are soluble in water; all are soluble in mineral acids, including H_3AsO_4. (See also under the respective metals.)

Arsenious sulfide, As_2S_3, is insoluble in water when prepared in the dry way; when prepared in the moist way it may become colloidal[6] upon treatment with pure water. It is reprecipitated by solutions of most inorganic salts. The presence of acids or salts prevents the solution of As_2S_3 in water. Boiling water slowly decomposes the sulfide forming As_2O_3 and H_2S. It is completely decomposed by gaseous HCl forming $AsCl_3$; very slightly decomposed by the hot concentrated acid. Chlorine water, hypochlorite, HNO_3, and aqua regia decompose it readily with formation of H_3AsO_4; with H_2SO_4, As_2O_3 and SO_2 are formed.

$$3\ As_2S_3 + 10\ HNO_3 + 4\ H_2O = 6\ H_3AsO_4 + 9\ S + 10\ NO$$

$$As_2S_3 + 5\ Cl_2 + 8\ H_2O = 2\ H_3AsO_4 + 3\ S + 10\ HCl$$

$$As_2S_3 + 14\ Cl_2 + 20\ H_2O = 2\ H_3AsO_4 + 3\ H_2SO_4 + 28\ HCl$$

$$As_2S_3 + 14\ HClO + 6\ H_2O = 2\ H_3AsO_4 + 3\ H_2SO_4 + 14\ HCl$$

The alkali hydroxides or carbonates dissolve it readily with the formation of $MAsO_2$ and $MAsS_2$, soluble in alkali sulfides and polysulfides forming $M_4As_2S_5$ and $MAsS_2$.[7] Freshly precipitated As_2S_3 is soluble in

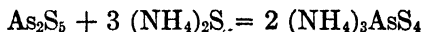
[1] Adie, *J. Ch. Soc. (Proc.)*, **15**, 133 (1899).
[2] Cf. Elsey, *Science*, [N.S.] **66**, 300 (1927).
[3] Anderson and Story, *J. Am. Ch. Soc.*, **45**, 1102 (1923).
[4] Vanzetti, *Gazz. ch. ital.*, **55**, 110–8 (1925).
[5] Menzies and Potter, *J. Am Ch. Soc.*, **34**, 1452 (1912).
[6] See Mellor, IX, 278–86.
[7] On the constitution of thioarsenites see: Wünschendorff, *Bull. soc. ch.*, **45**, 889–97 (1929); *C.A.* **24**, 1815.

alkali bisulfites, e.g., $NaHSO_3$ (separation from Sb and Sn);

$$2\,As_2S_3 + 16\,NaHSO_3 = 4\,NaAsO_2 + 6\,Na_2S_2O_3 + 3\,S + 7\,SO_2 + 8\,H_2O$$ [1]

readily soluble in $NH_4OH + H_2O_2$ giving $(NH_4)_3AsO_4$ and $(NH_4)_2SO_4$.[2] Arsenic sulfide, As_2S_5, is insoluble in water; volatilized in HCl gas, as $AsCl_3$; insoluble in dilute HCl; soluble in HNO_3, or chlorine water, as H_3AsO_4; soluble in alkali hydroxides, carbonates and sulfides with the formation of arsenates and thioarsenates (small amounts of sulfoxyarsenates, Na_3AsO_3S, etc., are also formed):[3]

$$4\,As_2S_5 + 24\,NaOH = 5\,Na_3AsS_4 + 3\,Na_3AsO_4 + 12\,H_2O$$

$$As_2S_5 + 3\,(NH_4)_2S = 2\,(NH_4)_3AsS_4$$

Arsenious chloride, bromide and iodide ($AsCl_3$, $AsBr_3$, AsI_3) are decomposed by small amounts of water into the corresponding oxyhalide, e.g., AsOCl. A further addition of H_2O decomposes these compounds into As_2O_3 and the halogen acid.

6. Reactions. — *a.* The alkali hydroxides and carbonates unite with arsenious and arsenic oxides forming soluble alkali arsenites and arsenates. These salts are chiefly meta-arsenites, e.g., $Na_4As_2O_5$, and orthoarsenates, e.g., Na_3AsO_4.

b. Oxalic acid does not reduce arsenic acid. Potassium ferricyanide in alkaline solution oxidizes arsenious compounds to arsenic compounds, very rapidly when gently warmed.

c. Nitric acid readily oxidizes all other compounds of arsenic to arsenic acid.

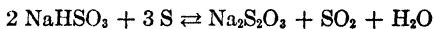
d. Hypophosphites, in presence of concentrated HCl, reduce all oxygen compounds of arsenic to the metallic state. Boiling a solution containing 0.1 mg. of arsenic with 10 cc. of concentrated HCl and 0.2 g. of calcium hypophosphite will give a good test[4] (6′, *f*).

e. Hydrosulfic acid precipitates lemon-yellow[5] arsenious sulfide, As_2S_3, from acid but not from alkaline solutions of arsenites. The precipitate forms in the presence of concentrated HCl. Citric acid and other organic compounds hinder formation of the precipitate, but do not wholly prevent it if strong HCl is present.

In aqueous solutions of arsenious acid the sulfide tends to become col-

[1] This equation somewhat arbitrarily combines the two reactions:

$$2\,As_2S_3 + 3\,NaHSO_3 = 3\,NaAsO_2 + 2\,HAsO_2 + 9\,S + H_2O$$

$$2\,NaHSO_3 + 3\,S \rightleftarrows Na_2S_2O_3 + SO_2 + H_2O$$

[2] For complex salts of As_2S_3 see Mellor, IX, 289–305.

[3] For the complex salts of As_2S_5 see Mellor, IX, 315–32.

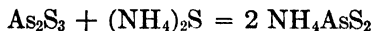
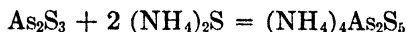
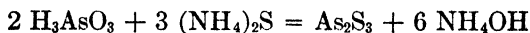
[4] Engel and Bernard, *Compt. rend.*, **122**, 390 (1896); Matthes, *Pharm. Ztg.*, **71**, 1508–9, 1543 (1926).

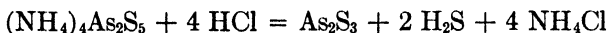
[5] Cf. Weiser, *J. Phys. Ch.*, **34**, 1021–32 (1930); *C.A.* **24**, 4199.

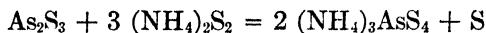
loidal (see 5, *c* above), decomposing when the solution is boiled: $As_2S_3 + 3\ H_2O = As_2O_3 + 3\ H_2S$. Alkali sulfides produce and, upon addition of excess, dissolve the precipitate (5, *c*):

$$2\ H_3AsO_3 + 3\ (NH_4)_2S = As_2S_3 + 6\ NH_4OH$$

$$As_2S_3 + 2\ (NH_4)_2S = (NH_4)_4As_2S_5$$

$$As_2S_3 + (NH_4)_2S = 2\ NH_4AsS_2$$

Arsenious sulfide is also soluble in alkali hydroxides and carbonates forming arsenites and thioarsenites (5, *c*). The thioarsenites react with acids forming As_2S_3:

$$(NH_4)_4As_2S_5 + 4\ HCl = As_2S_3 + 2\ H_2S + 4\ NH_4Cl$$

The solubility of the sulfides of arsenic in yellow ammonium sulfide, $(NH_4)_2S_2$, separates arsenic with antimony and tin from the other more common metals of the second group. As_2S_3 is oxidized in this reaction:

$$As_2S_3 + 3\ (NH_4)_2S_2 = 2\ (NH_4)_3AsS_4 + S$$

It may also be separated from antimony and tin by boiling with concentrated HCl, As_2S_3 remaining practically insoluble while the sulfides of antimony and tin dissolve.

Arsenic pentasulfide, As_2S_5, is formed by passing H_2S into a strongly acid solution of arsenic acid:

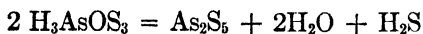
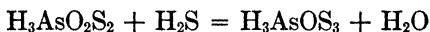
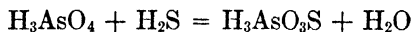
$$2\ H_3AsO_4 + 5\ H_2S\ (+\ HCl^1) = 2\ As_2S_5 + 8\ H_2O$$

The reaction may be considered to take place in steps as follows:

$$H_3AsO_4 + H_2S = H_3AsO_3S + H_2O$$

$$H_3AsO_3S + H_2S = H_3AsO_2S_2 + H_2O$$

$$H_3AsO_2S_2 + H_2S = H_3AsOS_3 + H_2O$$

$$2\ H_3AsOS_3 = As_2S_5 + 2H_2O + H_2S$$

To a slight extent the monosulphoxyarsenic acid first formed may decompose into arsenious acid and sulfur, with subsequent precipitation of As_2S_3.[2] $(NH_4)_2S$ added to a neutral or alkaline solution of arsenic acid forms ammonium thioarsenate, $(NH_4)_3AsS_4$. The addition of acid at once forms arsenic sulfide, As_2S_5. The reaction is more rapid than with H_2S and is facilitated by warming.

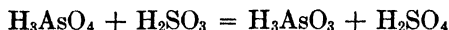
[1] The HCl acts as a coagulating agent.

[2] McCay, *Am. Ch. J.*, **10**, 459 (1888), *Z. anorg. allgem. Ch.*, **29**, 36 (1901); McCay and Foster, *Z. anorg. allgem. Ch.*, **41**, 452 (1904); Foster, *J. Am. Ch. Soc.*, **38**, 52 (1916), cf. Usher and Travers, *J. Ch. Soc.*, **87**, 1370 (1905); Foerster, *Z. anorg. allgem. Ch.*, **188**, 90–113 (1930), (Schenck, Festschr.); *C.A.* **24**, 2660.

Acid solutions of arsenites or arsenates when boiled with sodium thiosulfate form As_2S_3 and As_2S_5 respectively.[1] Arsenic may be removed from sulfuric acid by boiling with barium thiosulfate. No foreign material is introduced into the acid:

$$As_2O_3 + 3\ BaS_2O_3 = As_2S_3 + 3\ BaSO_4$$
$$2\ H_3AsO_4 + 5\ BaS_2O_3 = As_2S_5 + 5\ BaSO_4 + 3\ H_2O$$

Sulfurous acid readily reduces arsenic acid to arsenious acid:

$$H_3AsO_4 + H_2SO_3 = H_3AsO_3 + H_2SO_4$$

f. When tervalent and quinquivalent arsenic are treated with HF and H_2SO_4 only the tervalent arsenic is volatilized.[2] Treated with concentrated HCl[3] and then distilled in a current of HCl gas arsenic passes into the distillate as arsenious chloride, $AsCl_3$, pentavalent arsenic being slowly reduced.[4] Nearly all of the arsenic will be carried over in the first 50 cc. of the distillate. This is a very accurate quantitative separation of arsenic from all other metals except germanium, and from other non-volatile organic and inorganic material. The $AsCl_3$ should be distilled from a dilute solution at a temperature below 108° (to avoid contamination by Sb, $SnCl_4$ or $HgCl_2$) and absorbed in water. The solution thus obtained may be tested for AsO_3^{-3} by any of the usual methods (cf. 8). If it is necessary to recover the arsenic from the HCl solution this can readily be accomplished by adding a slight excess of hypochlorite, forming Cl_2, H_2O and AsO_4^{-3}. The chlorine can be removed by evaporation.[5]

Hydrobromic acid, in dilute solutions, is without action upon the acids of arsenic. The concentrated acid reduces H_3AsO_4 to H_3AsO_3: $H_3AsO_4 + 2\ HBr = H_3AsO_3 + Br_2 + H_2O$. Hydriodic acid reduces H_3AsO_4 to H_3AsO_3 with liberation of I_2.[6] This is a method for detection of As^{+5} in the presence of As^{+3}. As little as 0.1 mg. of arsenate may be detected in the presence of 1 g. of As_2O_3: $H_3AsO_4 + 2\ HI = H_3AsO_3 + I_2 + H_2O$.

Chloric and bromic acids oxidize As^{+3} to As^{+5} with formation of the corresponding hydracid: $3\ As_2O_3 + 2\ HBrO_3 + 9\ H_2O = 6\ H_3AsO_4 +$

[1] Vortmann, *Ber.*, **22**, 2307 (1889). See also Forbes and Walker, *Science*, **50**, 443–4 (1919), who found several intermediates as trithionate, pentathionate and sulfite when an excess of thiosulfate was used to precipitate As^{+5} in an HCl solution.

[2] Allen and Zies, *J. Am. Cer. Soc.*, **1**, 741 (1918).

[3] Smart and Philpot, *J. Soc. Chem. Ind.*, **33**, 900–12 (1914).

[4] Usually hydrazine, cuprous chloride, or other reducing agent is added to facilitate this reaction.

[5] For a discussion of the loss in qualitative analysis due to the volatility of $AsCl_3$, see Hinds, *Eighth Intern. Cong. Appl. Ch.*, **1**, 227–31 (1912).

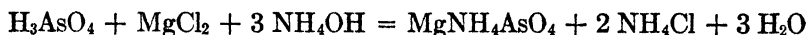
[6] Cf. Bobtelsky and Rosowskaja-Rossienskaja, *Z. anorg. allgem. Ch.*, **190**, 346–52 (1930); *C.A.* **24**, 4981.

2 HBr. Iodic acid oxidizes As^{+3} to As^{+5} with liberation of iodine: $5\ As_2O_3 + 4\ HIO_3 + 13\ H_2O = 10\ H_3AsO_4 + 2\ I_2$.

g. Stannous chloride[1] reduces all compounds of arsenic in hot, concentrated HCl to metallic arsenic, flocculent, dark brown. The $SnCl_2$ should be freshly prepared and the concentration of HCl over 25% for rapid and complete precipitation: $4\ AsCl_3 + 6\ SnCl_2 = As_4 + 6\ SnCl_2$. This is known as Bettendorff's test. Mercury interferes giving a gray precipitate capable of being gathered into globules. Antimony is not reduced by $SnCl_2$. Organic matter lowers the delicacy of the test but does not prevent it.

h. Chromates boiled with arsenites and $NaHCO_3$ give chromium arsenate.

i. Magnesium salts with NH_4Cl and NH_4OH precipitate from solutions of arsenates, magnesium ammonium arsenate, $MgNH_4AsO_4 \cdot 6H_2O$, white, crystalline, easily soluble in acids:

$$H_3AsO_4 + MgCl_2 + 3\ NH_4OH = MgNH_4AsO_4 + 2\ NH_4Cl + 3\ H_2O$$

The reagents should first be mixed, and the clear solution ("magnesia mixture") used, to make sure that enough ammonium salt is present to prevent the precipitation of $Mg(OH)_2$. The crystalline precipitate forms slowly but the separation is ultimately complete. (Compare with the corresponding magnesium ammonium phosphate: §189, 6, *d*.) Magnesium arsenite is insoluble in water, soluble in NH_4OH and in NH_4Cl (distinction from arsenate).

j. Silver nitrate solution precipitates from neutral solutions of arsenites, or silver-ammonia nitrate, $Ag(NH_3)_2NO_3$,[2] precipitates from an aqueous solution of As_2O_3, silver arsenite, Ag_3AsO_3, bright yellow, readily soluble in dilute acids or in NH_4OH (§59, 6, *g*). Arsenates are precipitated in neutral solution as silver arsenate, Ag_3AsO_4, reddish brown, having the same solubilities as the arsenite.

k. Copper sulfate solution precipitates from neutral solutions of arsenites, green copper arsenite, $Cu_3(AsO_3)_2 \cdot xH_2O$[3] (Scheele's green), soluble in NH_4OH and dilute acids. Copper acetate, in boiling solution, precipitates the green copper aceto-arsenite, $Cu(C_2H_3O_2)_2 \cdot 3Cu_2As_2O_5$[4] (Schweinfurt green), soluble in NH_4OH and acids. Both of these salts are designated as Paris green (§77, 6, *g*). With excess of free alkali[5] $CuSO_4$

[1] Durrant, *J. Ch. Soc.*, **115**, 134–43 (1919), discusses the interaction of $SnCl_2$ and $AsCl_3$.

[2] Prepared by adding NH_4OH to a solution of $AgNO_3$ until the brown precipitate at first produced has dissolved. Excess NH_4OH must be avoided.

[3] Composition varies with mode of preparation: Bornemann, *Z. anorg. allgem. Ch.*, **124**, 36 (1922).

[4] Schiff and Sestini, *Ann.*, **228**, 72 (1885).

[5] Kato and Murakami, *J. Soc. Ch. Ind.* (*Japan*), **33**, Suppl. binding, 226–7 (1930), state that the velocity of oxidation of AsO_3^{-3} to AsO_4^{-3} is almost proportional to the amount of NaOH present.

is reduced to Cu_2O with formation of alkali arsenate (cf. 10): $Na_3AsO_3 + 2\ CuSO_4 + 4\ NaOH = Na_3AsO_4 + 2\ Na_2SO_4 + Cu_2O + 2\ H_2O$. This is the basis for the Fehling's solution test for arsenite.[1] Copper arsenate, $Cu_3(AsO_4)_2$, greenish blue, is precipitated by $CuSO_4$ from solutions of arsenates, the solubility and conditions of precipitation being the same as for arsenites.

l. Ferric salts precipitate from arsenites — and freshly precipitated $Fe(OH)_3$ forms with As_2O_3 — variable basic ferric arsenites, scarcely soluble in acetic acid, soluble in HCl.[2] Water slowly and sparingly dissolves the As_2O_3 from the precipitate; but a large excess of $Fe(OH)_3$ will retain nearly all of the arsenic.[3] To some extent the basic ferric arsenites change to basic ferrous arsenates, insoluble in water, in accordance with the reducing power of As_2O_3. Arsenic acid or acid solutions of arsenates, in the presence of alkali acetates, yield with ferric salts ferric arsenate, $FeAsO_4$,[4] yellowish white, insoluble in acetic acid (compare §126, 6, *d*).

m. Ammonium molybdate, $(NH_4)_2MoO_4$,[5] in a nitric acid solution, when warmed (60°–70°) with a solution of an arsenate gives a yellow precipitate of ammonium arsenomolybdate, $(NH_4)_3AsO_4{\cdot}12MoO_3$. This precipitate is very similar in appearance and properties to ammonium phosphomolybdate, except that the latter precipitates in the cold. The limit of sensitivity is claimed to be one in 100 million. No precipitate is formed with AsO_3^{-3}.

6′. Special Reactions. — Special tests have been developed chiefly for the detection of small amounts of arsenic. The procedure is generally simple and rapid. Where preliminary concentration or purification is necessary the former may be effected by distillation from concentrated HCl (6, *f*). If the problem involves removal of organic matter several methods have been proposed:

(1) Method of Fresenius and Babo. — The finely divided sample[6] is treated with an equal weight of concentrated HCl and then 5–6 times as much water. The mass is heated on a water bath, small amounts of $KClO_3$ being added from time to time with stirring until a clear yellow liquid is obtained. The heating is continued until there is no odor of chlorine but evaporation should be avoided by the addition of water. The solution should be cooled and filtered, the arsenic being in the filtrate as

[1] For the history of this test see Cattelain, *J. pharm. ch.*, [8] **10**, 405–13, 449–58 (1929); *C.A.* **24**, 3193.

[2] Cf. Jellinek and Winogradoff, *Z. Elektroch.*, **30**, 477–90 (1924).

[3] There are reasons for believing that the product obtained as indicated above is not a compound but an adsorption product.

[4] Metzke, *Z. anorg. allgem. Ch.*, **19**, 457 (1899).

[5] For a color test using ammonium molybdate see: Denigès, *Compt. rend.*, **185**, 777–9 (1927); Feigl, *Ch. Ztg.*, **47**, 561 (1923).

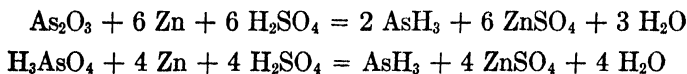
[6] Free from ammonium salts, otherwise there is danger of the formation of the very explosive nitrogen chloride, NCl_3, when the sample is treated with HCl and $KClO_3$.

arsenic acid. This may be reduced, e.g., with SO_2, and the arsenic precipitated as As_2S_3 or the arsenic removed by distillation (6, *f*) or other means.

(2) Method of Danger and Flandin. — The organic matter may be destroyed by heating in a porcelain dish with about one-fourth its weight of concentrated H_2SO_4. When the mass becomes dry and carbonaceous it is cooled, treated with concentrated HNO_3 and evaporated to dryness. The residue is moistened with water and HNO_3, and again evaporated to dryness. Repeat until the residue is colorless. Dissolve in water and test for arsenic. This method is objectionable if chlorides are present due to the possible formation of volatile $AsCl_3$.[1]

a. Marsh's Test.[2] — Arsenic, from all of its soluble compounds, is reduced by "nascent" hydrogen in acid solution to arsine, AsH_3, a colorless gas with garlic-like odor:

$$As_2O_3 + 6\ Zn + 6\ H_2SO_4 = 2\ AsH_3 + 6\ ZnSO_4 + 3\ H_2O$$

$$H_3AsO_4 + 4\ Zn + 4\ H_2SO_4 = AsH_3 + 4\ ZnSO_4 + 4\ H_2O$$

Arsine decomposes upon heating to form metallic arsenic (the so-called "arsenic mirror"), $4\ AsH_3 + \text{heat} \rightarrow As_4 + 6\ H_2$; and burns in air with a bluish flame, $4\ AsH_3 + 3\ O_2 = As_4 + 6\ H_2O$; $2\ AsH_3 + 3\ O_2 = As_2O_3 + 6\ H_2O$. The apparatus employed for these operations may be simple or complex depending upon the objective. The essential parts are an evolution flask, a purifying train, and a decomposition tube. The evolution flask is of the Erlenmeyer or Florence type, about 125 cc. in capacity, fitted with a rubber stopper having two holes through one of which passes a funnel (safety) tube reaching nearly to the bottom of the flask; the other holds a 5–7 mm. glass tube bent to a right angle. The end passing through the stopper should not extend beyond the bottom of the stopper, the other end is attached to a U-tube filled with glass wool moist — not wet — with $Pb(C_2H_3O_2)_2$ solution to absorb any H_2S evolved. (It has been claimed that the delicacy of the test is thus lowered in that the arsine reacts with the $Pb(C_2H_3O_2)_2$). Next comes a calcium chloride tube filled with about 8 mesh, anhydrous $CaCl_2$ or other suitable drying agent. Lastly a hard glass tube about 7 mm. in diameter by 25 cm. long is attached to the drying tube. This tube is constricted twice near the middle to about 2 mm. diameter, the distance between constrictions being 6–8 cm. The end of the tube is pulled out and turned up to form a tip suitable for

[1] For more detailed directions concerning the detection and estimation of arsenic in organic matter, special works on Toxicology, Forensic Chemistry and Legal Medicine should be consulted.

[2] Marsh, *Edinburgh N. Phil. J.*, **1836**, 229; *Rep. Pharm.*, **9**, 220 (1837). Lockemann, *Ch. Ztg.*, **36**, 1465–6 (1912), gives a history of Marsh's test. For a more complete discussion of the test see Rüdisüle, I, 9–23; VI, 2, 1216–23.

burning the exit gases.[1] A short piece of rubber tubing should be available for connecting this constricted end to a piece of ordinary glass tubing dipping into a test tube about two-thirds filled with a 2% solution of $AgNO_3$.

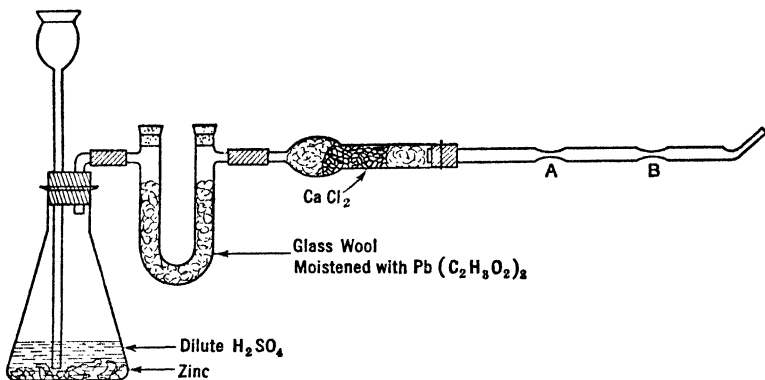



FIG. 1. Schematic Diagram of Marsh Test Apparatus.

Fifteen grams of granulated zinc[2] are placed in the flask with sufficient water to cover the end of the funnel tube and the stopper tightly fitted in place. Dilute H_2SO_4 (1 : 3) should now be added until a moderate evolution of hydrogen is obtained. The gas, allowed to bubble through $AgNO_3$ solution for several minutes, should produce no appreciable black precipitate or suspension, proving the system free from a large amount of arsenic, $6\ AgNO_3 + AsH_3 + 3\ H_2O = 6\ Ag + H_3AsO_3 + 6\ HNO_3$. The purity of the reagents having been established, the solution to be tested is added in small amounts at a time through the funnel tube. If much arsenic is present there will be an almost immediate blackening of the $AgNO_3$ solution. In case of doubt the hard glass tube should be heated[3] (at A) to just below the softening temperature.

The heat decomposes the arsine and a "mirror" of metallic arsenic is de-

[1] Obviously for careful work sulfur-vulcanized rubber (see 2, p. 194) connections should not be used and only arsenic free glass should be employed. Cf. Lockemann, *Z. angew. Ch.*, **18**, 427, 491 (1905).

[2] All reagents must be strictly arsenic free. Pure zinc is but slowly attacked by the acid and the flow of hydrogen is uneven. To avoid this difficulty Hefti tried zinc alloyed with 10% platinum, also zinc containing a very little copper. (Hefti, Dissertation, Zurich, 1907.) The latter is preferred. Direct addition of copper salts, e.g., $CuSO_4$, may cause loss of arsenic (Lockemann, *loc. cit.*), as may also platinochloride [Harkins, *J. Am. Ch. Soc.*, **32**, 518–30 (1910)]. Cf. Fresenius, *Z. anal. Ch.*, **45**, 767–8 (1906); Chapman and Law, *Analyst*, **31**, 3 (1906).

[3] Be sure that the apparatus is free from oxygen. As an additional precaution it is well to wrap a towel around the evolution flask. It is customary also to wrap a few turns of wire gauze around the portion of the tube receiving the heat.

posited in the cooler, less constricted portion of the tube. (A second flame may be applied at B to insure complete decomposition.) When a satisfactory mirror has been obtained the flame is withdrawn, and, removing the rubber tube, the escaping gas[1] is ignited. It burns with a slightly luminous, bluish flame (distinction from hydrogen which is practically colorless); water vapor and arsenious oxide passing into the air.

If present in considerable quantity the white powder (As_2O_3) may be observed settling on a piece of black paper placed beneath the flame. If the cold surface of a porcelain dish be brought in contact with the flame incomplete oxidation takes place and lustrous black or brownish black spots of metallic arsenic are deposited on the porcelain. A number of spots should be obtained and the various tests for metallic arsenic applied. The arsenic in the $AgNO_3$ solution is present as arsenious acid and can be detected by the usual tests (6, *e*) after removing the excess $AgNO_3$ with dilute HCl.

Arsine.[2] To generate arsine, magnesium or iron may be used instead of zinc, and hydrochloric acid instead of sulfuric. Arsine cannot be formed in the presence of oxidizing agents as the halogens, HNO_3, chlorate, hypochlorite, etc. Arsine may be produced from arsenious compounds by nascent hydrogen generated in alkaline solution. Sodium amalgam,[3] Zn and NaOH, or Al and NaOH may be used as the reducing agent (see below, Fleitmann's test). Fixed alkali hydroxides in solution have no effect on arsine. Concentrated NH_4OH causes incomplete decomposition with the separation of arsenic. Ferrocyanides react slowly in neutral, rapidly in alkaline solution. Nitric acid oxidizes arsine to arsenic acid, $3\ AsH_3 + 8\ HNO_3 = 3\ H_3AsO_4 + 8\ NO + 4\ H_2O$, and may be used instead of $AgNO_3$ to effect a separation of arsine and stibine in the Marsh test. The nitric acid solution is evaporated to dryness and the residue thoroughly washed with water. Test the solution thus obtained for arsenic. Dissolve the residue in HCl or aqua regia and test for antimony with H_2S.

Nitrites[4] readily decompose arsine forming a gray crust of arsenic, $4\ AsH_3 + 12\ HNO_2 = As_4 + 12\ NO + 12\ H_2O$. Arsine does not combine with H_2S until heated to 230°, while stibine, SbH_3, combines at

[1] Arsine is exceedingly poisonous, inhalation of the pure gas being quickly fatal. Its dissemination in the air of the laboratory, even in the small portions which are not appreciably toxic, should be avoided. Furthermore, as arsine is recognized or determined, in its various analytical reactions, only by its decomposition, to permit it to escape undecomposed is so far to fail in the object of its production. The evolved gas should be run into $AgNO_3$ or burned.

[2] For preparation and properties of solid AsH_3 see: Weeks, *Ch. News*, **128**, 54 (1924); Stock *et al.*, *Ber.*, **41**, 1319 (1908); Reckleben *et al.*, *Z. anal. Ch.*, **46**, 671 (1907); **47**, 105 (1908).

[3] Sodium amalgam is conveniently prepared by adding (in small pieces at a time) one part of sodium to eight parts (by weight) of warm, dry mercury. When cold the amalgam becomes solid and is easily broken. It should be kept in well-stoppered bottles.

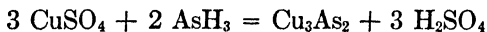
[4] Bozenhardt, *Apoth. Ztg.*, **21**, 580 (1906).

ordinary temperatures.[1] Sulfur dioxide forms As_4 and As_2S_3 at slightly elevated temperatures.

Concentrated sulfuric acid decomposes arsine at room temperature forming brown flakes which dissolve upon heating.

Hydrochloric acid[2] forms $AsCl_3$. (The removal of arsine from H_2S, by passing through hot, dilute HCl is incomplete.) Hypochlorites oxidize arsine to arsenate, $AsH_3 + 4\ NaClO = H_3AsO_4 + 4\ NaCl$. Chlorates or bromates with silver nitrate as a catalyst oxidize arsine to arsenate; iodic acid forms iodine and arsenic acid.

Salts of the heavy metals[3] in general decompose arsine. Silver nitrate, solid, forms $AsAg_3{\cdot}3AgNO_3$, yellow, $6\ AgNO_3 + AsH_3 = AsAg_3{\cdot}3AgNO_3 + 3\ HNO_3$, then metallic silver, $AsAg_3{\cdot}3AgNO_3 + 3\ H_2O = 6\ Ag + H_3AsO_3 + 3\ HNO_3$. If the silver nitrate is in solution the yellow compound is not obtained, $6\ AgNO_3 + AsH_3 + H_2O = 6\ Ag + 6\ HNO_3 + H_3AsO_3$.[4] With dry Hg_2Cl_2 or $HgCl_2$, solid, brown, mercurous arsenide, and HCl are formed.[5] Copper sulfate yields copper arsenide:

$$3\ CuSO_4 + 2\ AsH_3 = Cu_3As_2 + 3\ H_2SO_4$$

Gold salts form the metal;[6] zinc salts are slowly decomposed.

The most important interference in the Marsh test for arsenic is antimony which gives stibine, SbH_3, similar in many of its properties to arsine (see below). While germanium and selenium[7] also interfere they are so uncommon that the danger is negligible. Mercury, especially $HgCl_2$, should be absent,[8] also fluorides[9] and sulfites.[10] The latter form H_2S in the test, which in turn combines with arsine in the heated tube to give As_2S_3. In connection with the use of silver nitrate solution it is obvious that anything other than arsenic which gives a black precipitate must be avoided, e.g., sulfides, phosphorus compounds that would form phosphine, antimony compounds, bismuth, etc.

[1] Brunn, *Ber.*, **22**, 3202 (1889).

[2] For action of arsine on solutions of the halogens and halogen acids see: Reckleben and Lockemann, *Z. anal. Ch.*, **47**, 105–25 (1908).

[3] Reckleben, *et al.*, *Z. anal. Ch.*, **46**, 671–709 (1907). A report of the results of a long, elaborate investigation of the action of AsH_3 on solutions of salts of the heavy metals. Cf. Harkins, *J. Am. Ch. Soc.*, **32**, 518–30 (1910), who states that Fe, Hg, Pt, Ag, Pd, Ni, Co and their salts and large amounts of copper salts prevent complete evolution of arsenic as arsine; Sn, Bi, Cd and Pb, or their salts, have no injurious effects and their addition overcomes the effect of the others.

[4] Mellor, III, 22.

[5] Meissner, *Z. Expt. Path. Therap.*, **13**, 284 (1913).

[6] Güttlich, "Ueber Bestimmungsmethoden für Arsen- und Antimonwasserstoff," Leipzig, (1909).

[7] Meunier, *Compt. rend.*, **163**, 332–4 (1916); *Ann. ch. anal. ch. appl.*, **22**, 41–3 (1917).

[8] Vitali, *Boll. ch.-farm.*, **44**, 49–55 (1905).

[9] van Rijn, *Pharm. Weekblad*, **45**, 98–101 (1908).

[10] Smith, *Ch. News*, **83**, 2 (1901).

The delicacy of the Marsh test varies somewhat with the reagents employed. Using sulfuric acid and the Zn-Cu alloy, as little as 0.0_525 g. of As_2O_3 may be detected. On the other hand with tin and hydrochloric acid Vanino[1] found the limit to be 0.002 g. of As_2O_3.

Comparison of the mirrors and spots obtained with arsenic and antimony.

Arsenic Mirror	*Antimony Mirror*
Deposited beyond the flame; the gas not being decomposed much below a red heat.	Deposited before or on both sides of the flame; the gas being decomposed considerably below a red heat.
Sublimes below the softening point of the hard glass tube, allowing the mirror to be driven along the tube; it does not melt.	The mirror melts to minute globules and is then driven along at a red heat.
The vapor has a garlic-like odor.	The vapor has no odor.
By slow vaporization in a current of air a deposit of octahedral and tetrahedral crystals (of As_2O_3) is obtained, forming a white coating and giving the reactions for arsenious oxide.[2]	By vaporization in a current of air, a white amorphous coating is obtained; insoluble in H_2O, soluble in HCl and giving reactions for antimonous oxide.
Combines, when heated, with H_2S forming lemon-yellow As_2S_3, volatile and readily driven to the cooler portion of the tube. This dry sulfide is not readily attacked by dry HCl gas.	The heated mirror combines with H_2S forming orange Sb_2S_3, not readily volatile, easily decomposed by dry HCl gas forming $SbCl_3$ which is volatile and may be driven over the unattacked As_2S_3.

Arsenic Spots	*Antimony Spots*
A steel gray to black luster.	A velvety brown to black surface.
Volatile by oxidation to As_2O_3[3] below 300°.	Volatile by oxidation to Sb_2O_3 at a red heat.

[1] Vanino, *Z. angew. Ch.*, **15**, 857 (1902); Billeter, *Helv. Ch. Acta*, **6**, 258–9 (1923), offers a modification capable of detecting 0.0_52 mg. by distillation of $AsCl_3$, absorption in fuming HNO_3 and evaporation, the residue being tested in the Marsh apparatus.

[2] The tube containing the mirror may be cut, leaving about 5 cm. on each side of the mirror. Incline the tube and beginning at the lower edge of the mirror gently heat, driving it along the tube. The mirror will disappear, and if much arsenic be present a white powder will be seen forming a ring just above the heated portion of the tube. This powder consists of crystals of As_2O_3 and should be carefully examined under the microscope. Subsequently the crystals may be dissolved in water and tested for AsO_3^{-3} or in HNO_3 and tested for AsO_4^{-3}.

[3] Apparently a small amount of As_2O_5 is also formed.

Dissolve in hypochlorite.	Insoluble in hypochlorite.
Warmed with a drop of $(NH_4)_2S$ form yellow spots, soluble in $(NH_4)_2CO_3$, insoluble in HCl.	Warmed with $(NH_4)_2S$ form orange-yellow spots, insoluble in $(NH_4)_2CO_3$, soluble in HCl.
Dissolved by a drop of hot HNO_3. The clear solution with a drop of $AgNO_3$, when treated with NH_3 gives a brick red precipitate.	Turned white by a drop of hot HNO_3. The white fleck treated with $AgNO_3$ and NH_3, gives no color until warmed. Then a black precipitate is obtained with excess of the alkali.
The HNO_3 solution gives a yellow precipitate when warmed with a drop of ammonium molybdate.	With the white fleck (see above) no further action on addition of ammonium molybdate.
Iodine vapor produces a yellow AsI_3, readily volatile on heating.	Iodine vapor gives more or less carmine-red SbI_3, not readily volatile on heating.

b. Gutzeit Test.[1] This test is essentially a modification of Marsh's test, the chief differences being that (a) the arsine is detected by means of $AgNO_3$ or a mercuric salt, and (b) the apparatus may be a test tube.

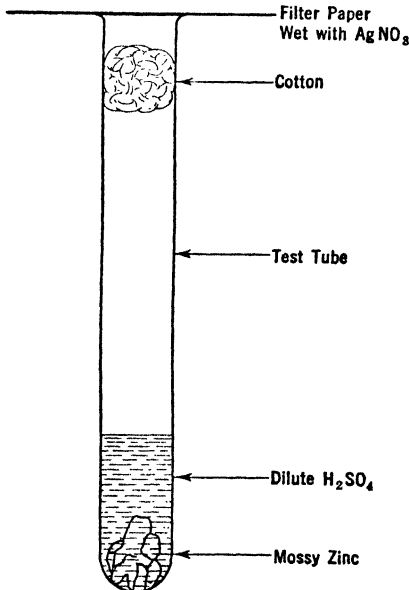



FIG. 2. Apparatus for the Gutzeit Test.

Place about 1 g. of granulated zinc in a 15 × 2.5 cm. test tube, add 4–5 cc. of dilute sulfuric acid (1 : 4) and a drop or two of cupric sulfate solution. Loosely plug the tube with cotton. Put a drop of lead acetate solution on the cotton (to detect sulfide) and then lay over the top of the tube a piece of filter paper moistened with silver nitrate solution. Warm the tube if necessary to produce an even flow of hydrogen. At the end of a definite length of time, e.g., 2 minutes, remove the filter paper and examine the part that covered the test tube. Usually a light brown spot will be observed due to traces of arsenic in the reagents. Remove the cotton plug and add 0.5–1 cc. of the solution to be tested. Quickly replace the plug and silver nitrate paper, the latter so that the new spot will be near, but not over, the first one. The rate of hydrogen evolution

[1] Gutzeit, *Pharm. Ztg.*, **24**, 263 (1879). For a complete summary and critical examination of the Gutzeit test see: Beckurts, *Pharm. Zentralhalle*, **25**, 197, 209, 223 (1884); Gotthelf, *Z. anal. Ch.*, **44**, 258 (1905).

being the same as before let the tube stand for an equal length of time. Now remove the filter paper and compare the two spots. If much arsenic is present the second spot will appear velvety black and have a distinct silvery sheen. If there is no noticeable difference between the two spots more of the solution may be added and the test repeated.

The interferences in this test are the same as those mentioned under Marsh's test (see above).[1] The precautions there listed are also applicable, though the danger of a serious explosion is not so great.

The sensitivity of the Gutzeit test as ordinarily conducted is somewhat lower than that of Marsh's test. Curtman and Daschavsky[2] state that using $AgNO_3$, a brown color is obtained if one part of arsenic in 150,000 is present. J. Cribier,[3] using $HgCl_2$ and intensifying with KI, found that he could detect 0.0001 mg. of arsenic. Many modifications and quantitative applications have been proposed.[4]

c. Fleitmann's Test,[5] involves the substitution of aluminum and sodium hydroxide for the zinc and sulfuric acid. In this way he avoids interference by antimony, etc. Arsenates do not give the test.

d. Reinsch's Test.[6] — If a solution of tervalent[7] arsenic be boiled with HCl and a strip of bright copper foil, the arsenic is deposited on the copper as a gray film. When a large amount of arsenic is present the coating separates from the copper in scales. The film does not consist of pure metallic arsenic, but appears to be copper arsenide, Cu_5As_2. The HCl should comprise at least 10% of the solution as arsenic is not deposited in the absence of the acid. This serves as a very satisfactory method for determining the presence or absence of arsenic in HCl. Dilute the concentrated acid with three parts of water and boil with a thin strip of bright copper foil. A trace of arsenic[8] if present will soon appear on the foil. For further identification of the deposit wash the foil with water, dry, and heat in a hard glass tube as for the oxidation of an arsenic mirror (Marsh's test). The white crystals of As_2O_3 are easily identified microscopically by their form. It is important that the surface of the copper should be bright. This is obtained by rubbing the foil with a file, pumice, or sandpaper just before using. The copper should not contain arsenic, but if a

[1] van Rijn, *Pharm. Weekblad,* **45**, 98–101 (1908), states that fluorides interfere in the Gutzeit but not in the Marsh test.

[2] Curtman and Daschavsky, *J. Am. Ch. Soc.,* **38**, 1280 (1916).

[3] Cribier, *J. pharm. ch.,* **24**, 241 (1921).

[4] See especially U. S. Pharmacopoeia X, 428.

[5] Fleitmann, *Ann.,* **77**, 126 (1851).

Dauvé, *Ann. ch. anal. ch. appl.,* **10**, 320–1 (1928), questions this test due to formation of SiH_4 which blackens $AgNO_3$ paper but not $HgCl_2$ paper.

[6] Reinsch, *J. prakt. Ch.,* **24**, 244 (1841); *Z. anal. Ch.,* **5**, 202 (1866); *Neues Jahrb. Pharm.,* **25**, 202 (1866). Leffman, *Analyst,* **55**, 684 (1930); *C.A.* **25**, 262 (historical).

[7] Quinquivalent arsenic is reduced far less readily.

[8] Paul and Cownley, *Pharm. J.,* **66**, 136 (1901), report a sensitivity of 1 : 250,000.

small amount is present no film will be deposited unless agents are present which cause solution of the foil, e.g., NO_3^-, ClO_3^-, Cl_2, etc. If a strip of the foil, upon boiling with HCl for 10 minutes, shows no dimming of the surface the purity of both acid and copper may be relied upon for the most exact work.[1] Sb, Hg, Ag, Bi, Pt, Pd and Au are deposited upon copper when boiled with HCl. Under certain conditions most of these deposits may closely resemble that of arsenic. Of these metals Hg is the only one that forms a sublimate when heated in the reduction tube (cf. 7). This is readily distinguished from arsenic by microscopic examination. Sb may be volatilized as an amorphous powder at a very high temperature. Selenium and sulfur interfere. Organic material may sometimes give a deposit on the copper which also yields a sublimate, but this is amorphous and does not show the octahedral crystals when examined under the microscope.[2]

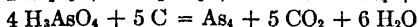
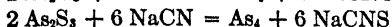
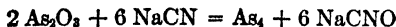
e. Bettendorff's Test.[3] — As indicated above (6, *g*), $SnCl_2$ in hot, concentrated HCl will reduce As^{+3} (As^{+5} slowly) to the metal. Winkler[4] claims that 0.0₄1 g. of As_2O_3 may be detected in this way. Sb, Sn, Pb, Cu and Cd do not interfere.[5] Sulfate may be reduced to H_2S, e.g., in the presence of bismuth, and cause the precipitation of SnS.[6] Zwicknagl[7] has shown that the most favorable conditions for the test are (1) concentrated HCl, (2) excess $SnCl_2$, (3) heat.[8]

f. Hypophosphite Test. — If a hypophosphite (6, *d*) be substituted for $SnCl_2$, metallic arsenic will be obtained, $4\ AsCl_3 + 3\ H_3PO_2 + 6\ H_2O = As_4 + 3\ H_3PO_4 + 12\ HCl$. If a small amount of arsenic is present only a yellowish-brown color will develop even upon prolonged heating. Using calcium hypophosphite a sensitivity to 0.1 mg. of As_2O_3 has been reported.[9]

g. In certain cases, e.g., presence of sulfur or nitrate, the sodium formate test[10] may be used to advantage. It involves the heating of a mixture of dry sodium formate with an arsenic compound to about 210°. The AsH_3 produced may be identified by methods already described.

7. Ignition. — Metallic arsenic is obtained by igniting any arsenic compound with sodium carbonate and charcoal, or with sodium cyanide:

[1] Paul and Cownley, *loc. cit.*
[2] Cf. Evans, *Analyst*, **48**, 357 (1923), for a study of the best conditions for detection of As, Sb and Bi.
[3] Bettendorff, *Z. anal. Ch.*, **9**, 105 (1870).
[4] Winkler, *Pharm. Zentralhalle*, **62**, 125 (1921).
[5] Scheucher, *Monatsh.*, **42**, 411–20 (1921).
[6] See however, Winkler, *Z. anal. Ch.*, **55**, 80 (1916).
[7] Zwicknagl, *Z. anorg. allgem. Ch.*, **151**, 41–52 (1926).
[8] See especially: Vanino and Hartwagner, *Arch. Pharm.*, **252**, 381–99 (1914), Mühe, *Z. anal. Ch.*, **55**, 358–63 (1916). The latter is a review.
[9] Rupp and Muschiol, *Ber. deut. pharm. Ges.*, **33**, 62 (1923). Cf. Deussen, *Arch. Pharm.*, **264**, 355–60 (1926), Kolthoff, *Pharm. Weekblad*, **59**, 334–50 (1922).
[10] Vournasos, *Ber.*, **43**, 2264 (1910).

$$2\,As_2O_3 + 6\,NaCN = As_4 + 6\,NaCNO$$
$$2\,As_2S_3 + 6\,NaCN = As_4 + 6\,NaCNS$$
$$2\,As_2S_3 + 6\,Na_2CO_3 + 6\,NaCN = As_4 + 6\,Na_2S + 6\,NaCNO + 6\,CO_2$$
$$4\,H_3AsO_4 + 5\,C = As_4 + 5\,CO_2 + 6\,H_2O$$

If the ignition is performed in a hard glass ignition tube the reduced arsenic sublimes and condenses as a mirror in the cool part of the tube. Fresenius and Babo especially recommend the method for the direct preparation of arsenic from As_2S_3. Performed in an atmosphere of CO_2 it is simple and accurate, and antimony does not interfere.

The test may be performed in the presence of Hg compounds, but more conveniently after their removal; in presence of organic material, it is unreliable. If much free sulfur is present the arsenic should be oxidized to arsenate by HNO_3 or by $HCl + KClO_3$, then precipitated, after addition of NH_4OH, by magnesia mixture, dried and mixed with the cyanide or other reducing agent.

8. Detection. — Arsenic is precipitated, from HCl solution, in the second group by H_2S as As_2S_3 or As_2S_5. Solution in $(NH_4)_2S_2$ separates it from Hg, Pb, Bi, Cu and Cd. The filtrate treated with dilute HCl gives a precipitate of As_2S_5, which, treated with concentrated HCl, is freed from Sb and Sn. The residue may be tested for arsenic by methods given in 6, 6′, and 7. For distinction between As^{+3} and As^{+5} see 6 and §88, 4. With the potassium salt of *o*-hydroxy-quinolin sulfonic acid, arsenate gives long needles soluble in acids and NH_4OH.[1, 2]

9. Determination.[3] — *Gravimetrically*, arsenic may be (1) precipitated as $MgNH_4AsO_4$ and weighed as $Mg_2As_2O_7$. This method is seldom employed. (2) It may be precipitated and weighed as As_2S_3. *Volumetrically*, arsenic may be quickly and easily determined in an HCl distillate by titration with $KBrO_3$ using methyl orange as an indicator. (3) It may be precipitated as Ag_3AsO_4 and the silver titrated with thiocyanate as in Volhard's method. (4) In neutral solution arsenite may be titrated with standard iodine, using starch as an indicator; or (5) KI may be used as the standard solution and the endpoint determined electrometrically. Arsenic cannot be determined electrolytically due to the formation of arsine. Small amounts of arsenic may be determined by precipitation as the metal using $SnCl_2$ or H_3PO_2 in concentrated HCl. The precipitate is dissolved in excess of standard iodine. Very small amounts of arsenic — 0.1 mg. or less — may be determined by volatilization as arsine and subsequent formation of an "arsenic mirror" (6′, *a*) or yellow complex with $HgBr_2$.[4]

10. Oxidation and Reduction. — As^{-3}, e.g., AsH_3, is oxidized to As^{+3} by $AgNO_3$, H_2SO_3, H_2SO_4 and HIO_3; and to As^{+5} by $KMnO_4$, HNO_2, HNO_3, Cl_2, ClO^-, Br_2 and BrO^-. As° is oxidized to As^{+3} by H_2O_2, HNO_3, H_2SO_4 hot, Cl_2, ClO^-, ClO_3^-, Br_2, BrO_3^-, IO_3^-, Ag^+, and to As^{+5} by the same reagents in excess except H_2SO_4 and Ag^+ which oxidize to As^{+3} only. As^{+3} is also oxidized to As^{+5} in presence of acid by PbO_2 and $Cr_2O_7^{--}$; by compounds of Co, Ni and Mn,[5] with valence greater than two; and in alkaline

[1] Schoorl, *Pharm. Weekblad*, **56**, 325 (1919).

[2] For other tests see: Gutzeit, *Helv. Ch. Acta*, **12**, 713–40 (1929); *C.A.* **23**, 4644

[3] A very complete discussion is given in Margosches, Vol. XVII–XVIII.

[4] U. S. Pharmacopoeia X, 428.

[5] Oryng, *Roczniki Ch.*, **7**, 334–44 (1927), *Z. anorg. allgem. Ch.*, **163**, 195 (1927); cf. *C.A.* **16**, 2439; **19**, 1998; **20**, 2442; **21**, 3574. Holluta, *Z. anorg. allgem. Ch.*, **168**, 361–8 (1928).

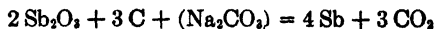
mixture by PbO_2, Hg_2O, HgO, CuO, K_2CrO_4, $K_3Fe(CN)_6$, ClO^-, etc. Arsine is oxidized to metallic arsenic by $HgCl_2$, and by As^{+3}, the latter also becoming As°. As^{+5} and As^{+3} are reduced to metallic arsenic by fusion with CO, with free carbon, or with combined carbon (C^{+4-n}), e.g., $H_2C_2O_4$, NaCN, etc.; by $SnCl_2$ (6, *g*) and H_3PO_2 (6, *d*) in strong HCl solution; by $Na_2S_2O_4$,[1] also with greater or less completeness by some free metals, such as Cu, Cd, Zn, Mg, etc. Rideal[2] has recommended the use of the Cu-Fe wire couple for the detection of small amounts of arsenic by reduction to the element — 0.0_575 g. may be detected. In solution As^{+5} is reduced to As^{+3} by H_3PO_2, H_2S, H_2SO_3, $Na_2S_2O_3$ (6, *e*), HCl, HBr, HI (6, *f*), $H_2C_2O_4$, HCNS, etc. As^{+5} and As^{+3} are reduced to As^{-3}, i.e., AsH_3, by nascent hydrogen generated by the interaction of Zn and H_2SO_4, or, in general, by any metal and acid which will readily generate hydrogen, as Zn, Sn, Fe, Mg, etc., with H_2SO_4 or HCl. As^{+3} is reduced to As^{-3} by nascent hydrogen generated in alkaline solution as from Al + NaOH, Zn + NaOH, sodium amalgam, etc. (separation from antimony).

§70. Antimony (L. *antimonium*) (Stibium). Sb = 121.76. Atomic No. 51. Valence 3 and 5. Discovered by Valentine in 1450.

1. Physical Properties. — Density, 6.70 at 22.3°;[3] melting point, 630.5°;[4] boiling point, 1440°.[5] Antimony is a lustrous silver-white, brittle and readily pulverizable metal. It is but little tarnished in dry air and oxidizes slowly in moist air, forming a dark gray mixture of antimony and antimonous oxide. At a red heat it burns in the air or in oxygen with incandescence, forming white inodorous (distinction from arsenic) vapors of antimonous oxide.

2. Occurrence. — Antimony is found chiefly as stibnite, Sb_2S_3. China has for many years been the world's largest producer, approximately 90% coming from this source in 1927. Mexico, Bolivia, Czechoslovakia and France each contribute a small amount. In 1928 the world's production was about 24,000 tons of metal, with a purity of at least 99%. In addition about 12,000 tons were recovered from old alloys, etc. Antimony is used chiefly in bearing metal alloys, type metal and — alloyed with lead — as storage battery plates. It has been stated that the average automobile contains about 3.5 pounds. The price in 1928 was 10 cents a pound.

3. Preparation. — (1) "Liquation." High grade ore is heated in a special furnace until the antimony sulfide melts and collects at the bottom. This "crude antimony" may be reduced by metallic iron ($Sb_2S_3 + 3\,Fe = 2\,Sb + 3\,FeS$) or converted to the oxide by roasting in air, and then reduced by fusion with coal or charcoal. (2) The sulfide is roasted and the Sb_2O_3 collected by sublimation. Reduction to the metal is effected by fusion with coal or charcoal and sodium carbonate:[6]

$$2\,Sb_2O_3 + 3\,C + (Na_2CO_3) = 4\,Sb + 3\,CO_2$$

[1] Staddon, *Ch. News*, **106**, 199 (1912).
[2] Rideal, *Ch. News*, **51**, 292 (1885).
[3] McAlpine, *J. Am. Ch. Soc.*, **51**, 1747 (1929).
[4] G. T. S., 1924.
[5] Greenwood, *Z. Elektroch.*, **18**, 319 (1912).
[6] Wang, *Trans. Am. Inst. Min. Eng.*, **60**, 3 (1919).

4. Oxides. — Antimony forms three oxides Sb_2O_3, Sb_2O_4, Sb_2O_5. (a) Antimonous oxide, Sb_2O_3, is formed (1) by the action of dilute nitric acid upon Sb°; (2) by treating a solution of $SbCl_3$ with Na_2CO_3 or NH_4OH; (3) by burning antimony at a red heat in air or oxygen (the product will contain some tetroxide); (4) by roasting the trisulfide (see 3 above). It is a white powder, turning yellow upon heating and white again when cooled; it melts at 656°.[1] At about 825° it absorbs O_2 from the air changing to the tetroxide. At higher temperatures (over 900°) this reaction is reversed. In the absence of air Sb_2O_3 volatilizes below 1550° without conversion to the tetroxide and forms a sublimate of needle-like crystals. Vapor density determinations indicate that the formula is Sb_4O_6. Antimonous oxide acts as an acid ($Sb_2O_3 + 2\,NaOH = 2\,NaSbO_2 + H_2O$) but more commonly as a base ($Sb_2O_3 + 6\,HCl = 2\,SbCl_3 + 3\,H_2O$). Ortho- and pyro-antimonous acids are known in the free state,[2] the meta form has been found only in its salts. (b) Antimony tetroxide, Sb_2O_4, is formed by heating Sb°, Sb_2S_3, Sb_2O_3 or Sb_2O_5 in air at 780–920°[3] for some time.[4] There are several theories as to the structure of antimony tetroxide; $SbSbO_4$ and $O = Sb - O - O - Sb = O$ are two of the formulas suggested.[5] Sb_2O_4 is found native as antimony ochre (cervantite). The artificial oxide is white; the mineral is white with a yellow to red tinge, also pale yellow. Above 900° the tetroxide decomposes to the trioxide. (c) Antimonic oxide, Sb_2O_5, is formed by treating Sb°, Sb_2O_3, or Sb_2O_4 with concentrated nitric acid.[6] When heated to 450°[7] it slowly loses oxygen, forming Sb_2O_4, at 800° the reaction is rapid ($2\,Sb_2O_5 = 2\,Sb_2O_4 + O_2$). It is a citron-yellow powder, reddening moist blue litmus paper. Antimonic acid exists in three forms[8] analogous to the arsenic and phosphoric acids. The ortho-acid, H_3SbO_4, is formed by the decomposition of $SbCl_5$ with water. A majority of the antimonates formed in the wet way by precipitation from the acid solution of $SbCl_5$ are the orthoantimonates. Heating the ortho-acid to 200°[9] gives the pyro-acid, $H_4Sb_2O_7$, which forms two series of salts $M_4Sb_2O_7$ and $M_2H_2Sb_2O_7$. The soluble potassium salt of the latter, $K_2H_2Sb_2O_7$[10] is used for the detection of sodium, $Na_2H_2Sb_2O_7$ being one of the few insoluble compounds of that element. The ortho- or pyro-acid heated to 300°[11] gives the meta-acid, $HSbO_3$. Strong ignition of Sb_2O_3 with KNO_3 and extraction with water gives potassium meta-antimonate, $KSbO_3$. The free acid is formed by adding HNO_3 to a solution of this salt.

5. Solubilities. — *a. Metal.* — Antimony is attacked but not dissolved by hot HNO_3[12] forming Sb_2O_3 (Eq. 1) or Sb_2O_5 (Eq. 2) depending upon the amount and concentration of the acid; it is slowly dissolved by hot, concentrated H_2SO_4, evolving SO_2 and forming $Sb_2(SO_4)_3$ (Eq. 3); it is insoluble in HCl out of contact with the air but the presence of moist air causes the oxidation of a small amount of the metal to Sb_2O_3 which dissolves in the acid without evolution of hydrogen.[13] The best solvent for antimony is HNO_3 followed by HCl, or nitrohydrochloric acid containing only a small amount of HNO_3. Antimonous chloride, $SbCl_3$, is first formed (Eq. 4), but if sufficient HNO_3 be present this is rapidly changed to antimonic chloride, $SbCl_5$ (Eq. 5). If, however, too much HNO_3 be present, the corresponding oxides are precipitated (6, *c*). A warm, dilute solution of HNO_3 and H_2F_2 is an excellent solvent for Sb° and its alloys. Nitric

[1] Quercigh, *Atti. accad. Lincei*, [5] **21**, i, 415 (1912).

[2] See also Simon and Poehlman, *Z. anorg. allgem. Ch.*, **149**, 101–24 (1925).

[3] Simon and Thaler, *Ibid.*, **162**, 253–78 (1927).

[4] Cf. Szilàgyi, *Z. anal. Ch.*, **57**, 23 (1918).

[5] Mellor, IX, 434.

[6] Cf. Bošek, *J. Ch. Soc.*, **67**, 515 (1895).

[7] Biltz, *Z. physik. Ch.*, **19**, 385 (1896).

[8] Cf. Mellor, IX, 439; Tomula, *Z. anorg. allgem. Ch.*, **118**, 81–92 (1921); Jander, *Kolloid Z.*, **23**, 122–44 (1919).

[9] Senderens, *Bull. soc. ch.*, [3] **21**, 47 (1899).

[10] There seems to be some question concerning this compound. The formula may be KH_2SbO_4.

[11] Senderens, *loc. cit.*

[12] Antimony may be dissolved in HNO_3 if the temperature is properly regulated.

[13] $SbCl_3$ is lost by volatilization when boiled in HCl above 108°.

acid, in the presence of tartaric acid, readily dissolves antimony. Hydrochloric acid containing bromine is also a good solvent. The halogens readily attack the metal first forming the corresponding trihalogen compound (Eq. 4). Chlorine and bromine (gaseous) unite with the production of light, and if the chlorine be in excess, the pentachloride (Eq. 5) is formed. The pentabromide, $SbBr_5$, and penta-iodide, SbI_5, apparently have not been prepared.

(1) $2\,Sb + 2\,HNO_3 = Sb_2O_3 + 2\,NO + H_2O$
(2) $6\,Sb + 10\,HNO_3 = 3\,Sb_2O_5 + 10\,NO + 5\,H_2O$
(3) $2\,Sb + 6\,H_2SO_4 = Sb_2(SO_4)_3 + 3\,SO_2 + 6\,H_2O$
(4) $2\,Sb + 3\,Cl_2 = 2\,SbCl_3$
(5) $SbCl_3 + Cl_2 = SbCl_5$

b. Oxides. — Antimonous oxide, Sb_2O_3, dissolves in water at 15° to the extent of 0.018 g./l. It is soluble in HCl (Eq. 1), H_2SO_4 and tartaric acid (Eq. 2) with formation of the corresponding salts. The dry, ignited oxide is only slightly soluble in HNO_3; the moist, freshly precipitated oxide, however, dissolves readily in the dilute or concentrated acid, warm or cold. Under certain conditions of concentration a portion of the antimony separates upon standing as a white crystalline precipitate. It is soluble in the fixed alkali hydroxides with formation probably of ortho- or meta-antimonites (Eq. 3) depending upon the concentration of the alkali. Fixed alkali carbonates dissolve a small amount of the oxide with the probable formation of some antimonite (Eq. 4).[1] The oxide is fairly soluble in glycerine.

(1) $Sb_2O_3 + 6\,HCl = 2\,SbCl_3 + 3\,H_2O$
(2) $Sb_2O_3 + H_2C_4H_4O_6 = (SbO)_2C_4H_4O_6 + H_2O$
(3) $Sb_2O_3 + 2\,KOH = 2\,KSbO_2 + H_2O$
(4) $Sb_2O_3 + Na_2CO_3 = 2\,NaSbO_2 + CO_2$

Antimony tetroxide, Sb_2O_4, is insoluble in water, slowly dissolved by hot concentrated HCl, slightly soluble in H_2SO_4.

Antimonic oxide, Sb_2O_5, is insoluble in water; soluble in HCl[2] and tartaric acid without reduction; HI dissolves it as SbI_3 with liberation of iodine ($Sb_2O_5 + 10\,HI = 2\,SbI_3 + 5\,H_2O + 2\,I_2$); slowly soluble in concentrated fixed alkalis; soluble in alkaline solution of glycerine; slowly soluble in ammonium sulfide. The hydrated oxides, i.e., acids, have essentially the same solubilities as the oxides. The ortho-acid, H_3SbO_4, is sparingly soluble in water, easily soluble in KOH, but insoluble in NaOH due to the insolubility of the sodium antimonates. The meta-acid, $HSbO_3$, is sparingly soluble in water, easily soluble in the fixed alkalis. The pyro-acid, $H_4Sb_2O_7$, is more soluble in water than the meta-acid.

c. Salts. — Antimonous chloride, $SbCl_3$, is very deliquescent, decomposed by pure water forming SbOCl;[3] soluble in strong aqueous solutions of inorganic acids, also tartaric, citric or oxalic acids (6, *b*), but not acetic acid. It is also soluble in concentrated solutions of the alkali and alkaline earth chlorides. The bromide and iodide are deliquescent and require moderately concentrated acid to keep them in solution. The sulfate, $Sb_2(SO_4)_3$, dissolves in moderately concentrated H_2SO_4. Antimonous tartrate and potassium antimonyl tartrate (tartar emetic) $K(SbO)C_4H_4O_6\cdot\frac{1}{2}H_2O$ are soluble in water, the latter precipitates, from aqueous solution, SbOCl when treated with dilute HCl. The precipitate dissolves readily in excess acid (see above). Tartar emetic is also soluble in glycerine but

[1] See Mellor, IX, 428–33.
[2] Cf. Stelling, *Ind. Eng. Ch.*, **16**, 346 (1924).
[3] The composition apparently varies somewhat depending upon conditions.

insoluble in alcohol. The trichloride, bromide and iodide are soluble in hot CS_2; the chloride and bromide are soluble in alcohol without decomposition but the iodide is partially decomposed by alcohol or ether.

The pentachloride, $SbCl_5$, is a liquid, very readily combining with a small amount of water to form crystals containing one or four molecules of H_2O. The addition of more water decomposes the compound forming the basic salt; if, however, a little HCl is added first (forming $HSbCl_6$), any desired amount of water (if added at one time) may be introduced without causing immediate precipitation of the basic salt.

Antimonous sulfide, Sb_2S_3, is readily soluble in alkali sulfides (Eq. 1);[1] soluble in moderately concentrated HCl with evolution of H_2S (Eq. 2); slowly decomposed by boiling water into Sb_2O_3 and H_2S (Eq. 3), and on boiling with NH_4Cl into $SbCl_3$ and $(NH_4)_2S$.[2] Dilute H_2SO_4 is almost without action, dilute HNO_3 gives Sb_2O_3 (Eq. 4). Antimonous sulfide is sparingly soluble in hot NH_4OH, soluble in the fixed alkalis (on fusion or boiling) (Eq. 5); insoluble in $(NH_4)_2CO_3$ (distinction from As); insoluble in the fixed alkali carbonates in the cold but completely dissolved upon warming (Eq. 6) (distinction from Sn); slightly soluble in $(NH_4)_2S$; readily soluble in $(NH_4)_2S_2$ with oxidation (Eq. 7) (6, *e*). Solutions of the alkaline earth hydroxides form thioantimonites when boiled with Sb_2S_3. Antimonous sulfide is soluble in hot tartaric acid, slowly soluble in oxalic acid, soluble in citric acid, easily soluble in the last two if NO_3^-, NO_2^- or ClO_3^- be present. Solutions of $CuSO_4$, $HgCl_2$ and $FeCl_3$ (slightly acid) completely decompose Sb_2S_3.

The pentasulfide, Sb_2S_5, is insoluble in water; soluble in alkali sulfides (Eq. 8), and in the fixed alkali hydroxides (Eq. 9); insoluble in $(NH_4)_2CO_3$ and sparingly soluble in NH_4OH, more readily when warmed (boiling causes precipitation of Sb_2S_3 and S). On boiling with water Sb_2S_5 slowly decomposes into Sb_2O_3, H_2S and S; on warming with HCl it dissolves to form $SbCl_3$ (Eq. 10).

(1) $Sb_2S_3 + 2\ Na_2S = Na_4Sb_2S_5$

(2) $Sb_2S_3 + 6\ HCl = 2\ SbCl_3 + 3\ H_2S$

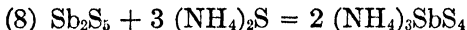
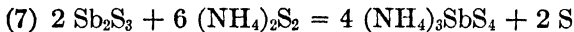
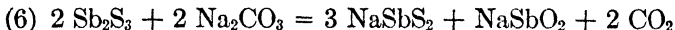
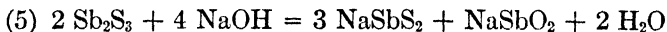
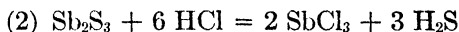
(3) $Sb_2S_3 + 3\ H_2O = Sb_2O_3 + 3\ H_2S$

(4) $Sb_2S_3 + 2\ HNO_3 = Sb_2O_3 + 3\ S + 2\ NO + H_2O$

(5) $2\ Sb_2S_3 + 4\ NaOH = 3\ NaSbS_2 + NaSbO_2 + 2\ H_2O$

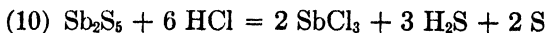
(6) $2\ Sb_2S_3 + 2\ Na_2CO_3 = 3\ NaSbS_2 + NaSbO_2 + 2\ CO_2$

(7) $2\ Sb_2S_3 + 6\ (NH_4)_2S_2 = 4\ (NH_4)_3SbS_4 + 2\ S$

(8) $Sb_2S_5 + 3\ (NH_4)_2S = 2\ (NH_4)_3SbS_4$

[1] A number of thioantimonites have been prepared. Mellor, IX, 532–6.

[2] Probably NH_3 and H_2S are also liberated, the reaction requiring a relatively high concentration of NH_4Cl.

(9)[1] $4\ Sb_2S_5 + 18\ NaOH = 5\ Na_3SbS_4 + 3\ NaSbO_3 + 9\ H_2O$

(10) $Sb_2S_5 + 6\ HCl = 2\ SbCl_3 + 3\ H_2S + 2\ S$

6. Reactions. — *Water.* — Excepting the fluoride and some organic compounds of antimony, e.g., tartrates and citrates, all salts of Sb are decomposed by pure water. The salts with inorganic acids all require the presence of some free acid (not acetic) to keep them in solution. If the acid be tartaric the further addition of H_2O causes no precipitation of the antimony salt. Water decomposes the inorganic acid solutions, except fluorides, precipitating the basic salt and liberating H^+ and Cl^- which prevent the reaction from going to completion. ($SbCl_3 + H_2O = SbOCl + 2\ H^+ + 2\ Cl^-$) (see below). The addition of more water, by mass action effect and dilution, causes nearly complete precipitation. If the precipitate be washed with water the acid is gradually displaced, leaving finally Sb_2O_3.

Solutions of $SbCl_3$ form, when diluted with H_2O, a series of oxychlorides from SbOCl to $Sb_4Cl_2O_5$[2] ("Powder of Algaroth") depending upon the amount of H_2O added. ($SbCl_3 + H_2O = SbOCl + 2\ HCl$; $4\ SbCl_3 + 5\ H_2O = Sb_4Cl_2O_5 + 10\ HCl$). The precipitate is soluble in tartaric acid (distinction from BiOCl) and does not form in presence of sufficient alkali or alkaline earth chloride. With $SbCl_5$ the basic salt is thought to be $SbOCl_3$, but this formula has been questioned.

a. The alkali hydroxides and carbonates precipitate from acidulated solutions of inorganic antimonous salts, antimonous oxide, Sb_2O_3 (Eq. 1) (or possibly an antimonite, e.g., $HSbO_2$), white, bulky, readily becoming crystalline on boiling, sparingly soluble in water, readily soluble in excess of the fixed alkalis[3] forming a meta-antimonite (Eq. 2), more or less soluble in an excess of the fixed alkali carbonates in hot solution (Eq. 3) (distinction from Sn), insoluble in NH_4OH or $(NH_4)_2CO_3$. Sodium antimonite, $NaSbO_2$, is the most stable and least soluble in water; potassium antimonite, $KSbO_2$, is readily soluble in dilute KOH solution, but decomposed by pure water. A portion of the Sb precipitates from the alkaline solution on long standing (24 hours), and the presence of alkali bicarbonates causes an almost complete separation of the oxide (Eq. 4). If an alkaline solution of Sb be carefully neutralized with an acid (not hydrofluoric, tartaric or citric) the oxide is precipitated (Eq. 5) and at once dissolved by further addition of acid. The presence of tartaric or citric acid prevents the precipitation of the oxide by means of the alkalis or alkali carbonates.

[1] Weinland and Lehmann, *Z. anorg. allgem. Ch.*, **26**, 343 (1901). L. W. McCay [*Am. Ch. J.*, **17**, 770 (1895)] suggests that the reaction with alkali hydroxide may be: $2\ Sb_2S_5 + 9\ KOH = 3\ K_2HSbO_2S_2 + K_3SbO_4 + 3\ H_2O$, followed by partial decomposition of the sulfoxyantimonate: $2\ K_2HSbO_2S_2 = KSbO_3 + K_3SbS_4 + H_2O$.

[2] Lea and Wood, *J. Ch. Soc.*, **123**, 259 (1923).

[3] Cormimboeuf, *Compt. rend.*, **115**, 1305 (1892).

(1) $2\ SbCl_3 + 6\ NaOH = Sb_2O_3 + 6\ NaCl + 3\ H_2O$

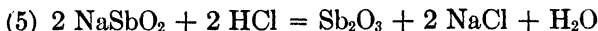
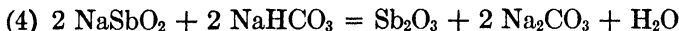
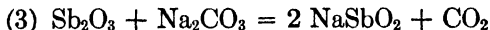
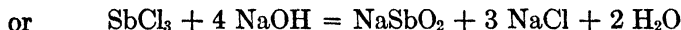
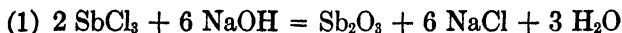
$2\ SbCl_3 + 3\ Na_2CO_3 = Sb_2O_3 + 6\ NaCl + 3\ CO_2$

(2) $Sb_2O_3 + 2\ NaOH = 2\ NaSbO_2 + H_2O$

or $SbCl_3 + 4\ NaOH = NaSbO_2 + 3\ NaCl + 2\ H_2O$

(3) $Sb_2O_3 + Na_2CO_3 = 2\ NaSbO_2 + CO_2$

(4) $2\ NaSbO_2 + 2\ NaHCO_3 = Sb_2O_3 + 2\ Na_2CO_3 + H_2O$

(5) $2\ NaSbO_2 + 2\ HCl = Sb_2O_3 + 2\ NaCl + H_2O$

Antimonic salts are precipitated under the same conditions as the antimonous salts. The freshly formed precipitate is orthoantimonic acid, $H_3SbO_4 = SbO(OH)_3 = Sb_2O_5{\cdot}3H_2O$ ($SbCl_5 + 5\ KOH = H_3SbO_4 + 5\ KCl + H_2O$); insoluble in NH_4OH or $(NH_4)_2CO_3$; soluble in excess of the fixed alkali hydroxides and carbonates. The sodium salt of pyroantimonic acid, $Na_2H_2Sb_2O_7$, is insoluble in water and may be formed in the quantitative estimation of Sb (cf. 9), also in a method for the detection of Na (§206, 6, *g*). For the latter the soluble potassium salt, $K_2H_2Sb_2O_7$ (or KH_2SbO_4), is used as the reagent. This compound must be kept dry, and dissolved when required for use. It changes in solution to $K_4Sb_2O_7$ which does not precipitate sodium. The reagent is, of course, not applicable in acid solutions. The reaction is: $K_2H_2Sb_2O_7 + 2\ NaCl = Na_2H_2Sb_2O_7 + 2\ KCl$, or $KH_2SbO_4 + NaCl = NaH_2SbO_4 + KCl$.

b. Freshly precipitated antimonous oxide is soluble in oxalic acid but the antimony soon slowly, but completely, separates as a white crystalline precipitate unless an alkali oxalate be present which promotes the formation of a soluble double oxalate.[1] The precipitate of antimony oxalate dissolves in HCl. Freshly precipitated antimonic oxide dissolves readily in oxalic acid and does not separate upon standing. Acetic acid produces a precipitate when added to solutions of antimony salts if tartaric acid be absent. KCN gives a white precipitate with antimonous salts, soluble in excess cyanide. With potassium ferrocyanide $SbCl_3$ gives a white precipitate, insoluble in HCl (distinction from Sn) or the fixed alkali hydroxides. Potassium ferricyanide does not give a precipitate in acid solution but is reduced to ferrocyanide by antimonous salts in alkaline solution.[2]

c. The oxides or hydrated oxides (acids) are precipitated from solutions of the fixed alkali antimonites or antimonates upon neutralization with HNO_3 or other inorganic acids, the freshly formed precipitate readily dissolving in an excess of the acid. Antimonous nitrate is very unstable and antimonic nitrate apparently has not been prepared. It is possible that

[1] Holmes and Turner, *J. Ch. Soc.*, **127**, 1753–4 (1925).
[2] Baumann, *Z. angew. Ch.*, **5**, 117 (1892).

the nitric acid solutions are solutions of the hydrated oxides (acids) and not the normal nitrates.

d. Compounds of antimony with the acids of phosphorus are not known.[1] Na_2HPO_4 does not precipitate antimony salts (separation from Sn).

e. Hydrosulfic acid, H_2S, precipitates from not too strongly acid solutions of Sb^{+3}, antimonous sulfide, Sb_2S_3, (Eq. 1) orange-red;[2] in neutral solution (tartrate present) the precipitation is incomplete. In fixed alkali solution (6, *a*) the precipitation is prevented, or any sulfide first formed (Eq. 2) reacts at once with the excess alkali (Eq. 3). NH_4OH has little effect. The alkali sulfides, e.g., Na_2S, give the same precipitate; sparingly soluble in $(NH_4)_2S$, readily soluble in the fixed alkali sulfides (Eq. 4) and in $(NH_4)_2S_2$ (Eq. 5). Sb_2S_3 is slowly decomposed by boiling H_2O (Eq. 6); insoluble in $(NH_4)_2CO_3$ (distinction from As); slowly soluble in boiling solutions of the fixed alkali carbonates (Eq. 7) (distinction from Sn); soluble in cold concentrated, and in hot 1 : 1 HCl (Eq. 8) (distinction from As). The thioantimonites are oxidized upon standing, by the oxygen of the air, rapidly in the presence of sulfur (Eq. 5); from the alkaline solutions HCl precipitates Sb_2S_3, Sb_2S_5, or a mixture, depending upon the state of oxidation (Eq. 9).

(1) $2\ SbCl_3 + 3\ H_2S = Sb_2S_3 + 6\ HCl$

(2) $2\ NaSbO_2 + 3\ H_2S = Sb_2S_3 + 2\ NaOH + 2\ H_2O$

(3) $2\ Sb_2S_3 + 4\ KOH = 3\ KSbS_2 + KSbO_2 + 2\ H_2O$

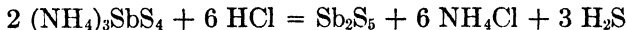
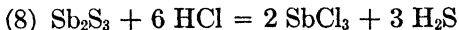
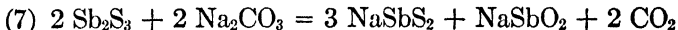
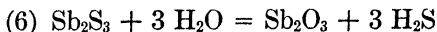
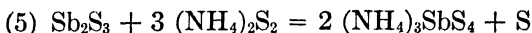
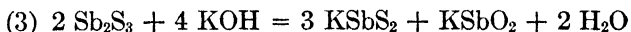
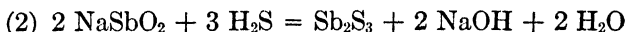
(4) $Sb_2S_3 + Na_2S = 2\ NaSbS_2$

(5) $Sb_2S_3 + 3\ (NH_4)_2S_2 = 2\ (NH_4)_3SbS_4 + S$

(6) $Sb_2S_3 + 3\ H_2O = Sb_2O_3 + 3\ H_2S$

(7) $2\ Sb_2S_3 + 2\ Na_2CO_3 = 3\ NaSbS_2 + NaSbO_2 + 2\ CO_2$

(8) $Sb_2S_3 + 6\ HCl = 2\ SbCl_3 + 3\ H_2S$

(9) $3\ KSbS_2 + KSbO_2 + 4\ HCl = 2\ Sb_2S_3 + 4\ KCl + 2\ H_2O$
$2\ (NH_4)_3SbS_4 + 6\ HCl = Sb_2S_5 + 6\ NH_4Cl + 3\ H_2S$

Hydrosulfic acid and alkali sulfides precipitate under conditions similar to those mentioned above, antimonic sulfide, Sb_2S_5,[3] orange, from solutions of antimonic salts. This sulfide has the same solubilities as the trisulfide except that Sb_2S_5 is soluble in NH_4OH. The thioantimonate solution consists chiefly of the orthoantimonate, instead of the meta- as in anti-

[1] Köhler, *Dingler's poly. J.*, **258**, 520 (1885) reports an antimonous phosphate.

[2] Upon boiling the red sulfide or upon passing H_2S into the hot solution for a long time, the black modification is obtained.

[3] Hock, *Kautschuk*, Dec., **1925**, pp. 11–13, offers evidence for the existence of Sb_2S_5; cf. Kirchhoff, *Z. anorg. allgem. Ch.*, **112**, 67–80 (1920).

monous compounds ($Sb_2S_5 + 3\ K_2S = 2\ K_3SbS_4$; $4\ Sb_2S_5 + 18\ KOH = 5\ K_3SbS_4 + 3\ KSbO_3 + 9\ H_2O$).[1] When dissolved in HCl the pentasulfide is reduced to $SbCl_3$ with liberation of sulfur, $Sb_2S_5 + 6\ HCl = 2\ SbCl_3 + 3\ H_2S + 2\ S$. All salts of antimony when boiled with $Na_2S_2O_3$[2] give precipitates of the sulfide[3] ($2\ SbCl_3 + 3\ Na_2S_2O_3 + 3\ H_2O = Sb_2S_3 + 3\ Na_2SO_4 + 6\ HCl$). Sulfurous acid reduces Sb^{+5} to Sb^{+3}. Sulfates of Sb are not prepared by precipitation, but by boiling the oxides with concentrated H_2SO_4. They are readily hydrolyzed by H_2O.

f. Hydrochloric acid, or any other inorganic acid, except HF, carefully added to a solution of Sb salts in the fixed alkalis will precipitate the corresponding oxide or hydrated oxide, soluble upon further addition of the acid (for HNO_3 see 5, *b* and 6, *c*). KI added to $SbCl_3$, not too strongly acid, gives a yellow precipitate of SbI_3, soluble in HCl. The precipitation does not take place in the presence of oxalic or tartaric acids. Apparently SbI_4 or SbI_5 have not been prepared.[4] HI (or KI in acid solution) added to a solution of Sb^{+5} causes a reduction of the antimony to Sb^{+3} with liberation of I_2[5] (distinction from Sn^{+4}), $SbCl_5 + 2\ HI = SbCl_3 + 2\ HCl + I_2$. The solution must be acid, for in alkaline solution the reverse action takes place, $SbCl_3 + 8\ NaOH + I_2 = Na_3SbO_4 + 2\ NaI + 3\ NaCl + 4\ H_2O$.

g. If antimony and arsenic compounds occurring together are treated with concentrated HNO_3, the precipitate of antimony oxide may contain arsenic, as antimonic arsenate. $SnCl_2$ reduces Sb^{+5} to Sb^{+3} but does not cause a precipitation of the metal (distinction from As).

h. Antimonous salts in acid, neutral or alkaline solution, rapidly reduce CrO_4^{--} or $Cr_2O_7^{--}$ to Cr^{+3}. Acid solutions of Sb^{+3} reduce MnO_4^{--} and MnO_4^- to Mn^{++}; in alkaline solution the product is MnO_2. The Sb^{+3} becomes Sb^{+5}. These reactions are capable of quantitative application in absence of other reducing agents.

i. An Sb^{+3} compound when evaporated on a water bath with $Ag(NH_3)_2NO_3$ gives a black precipitate. A solution of Sb^{+3} in fixed alkali when treated with $AgNO_3$ gives a heavy black precipitate of Ag, insoluble in NH_4OH, and thus separated from any Ag_2O precipitated. If, instead of $AgNO_3$, a solution of $Ag(NH_3)_2NO_3$ containing a large excess of NH_4OH (1 : 16) be added, no precipitation occurs in the cold (distinction from SnO_2^{--}); nor upon heating until the excess NH_3 has been driven off. Antimonates with $AgNO_3$ give a white precipitate of silver antimonate, $AgSbO_3$, soluble in NH_4OH before drying.

[1] See footnote to Eq. 9, p. 214.

[2] Szilàgyi, *Z. anorg. allgem. Ch.*, **113**, 69–74 (1920).

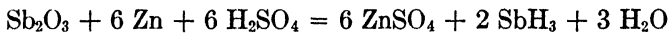
[3] Under certain conditions red "antimony vermillion," Sb_2S_3, containing some Sb_2O_3, is obtained.

[4] Ruff, *Ber.*, **48**, 2068–76 (1915).

[5] The iodine may be detected by adding carbon tetrachloride, CCl_4, and shaking.

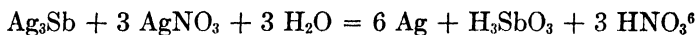
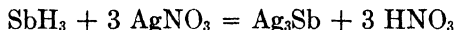
j. Stibine. — By the action of Zn and H_2SO_4 or HCl all compounds of antimony are first reduced to the metallic state. With moderately rapid generation of hydrogen some stibine, SbH_3, is formed[1] due to a secondary reaction.

$$Sb_2O_3 + 6\ Zn + 6\ H_2SO_4 = 6\ ZnSO_4 + 2\ SbH_3 + 3\ H_2O$$

$$SbCl_3 + 3\ Zn + 3\ HCl = 3\ ZnCl_2 + SbH_3$$

Stibine is a colorless, odorless gas more poisonous than arsine.[2] Stibine burns with a faintly bluish-green flame, forming antimonous oxide and water, $2\ SbH_3 + 3\ O_2 = Sb_2O_3 + 3\ H_2O$, or depositing Sb, on cold porcelain held in the flame, as a lusterless black spot, $4\ SbH_3 + 3\ O_2 = 4\ Sb + 6\ H_2O$. The gas is also decomposed by passing through a glass tube heated to a dull red, $2\ SbH_3 = 2\ Sb + 3\ H_2$. A lustrous ring or mirror is formed in the tube. The SbH_3 is decomposed more readily by heat than is AsH_3[3] and the mirror is deposited on both sides of the heated portion of the tube. The Sb in stibine is deposited as the metal when the gas is passed into a concentrated solution of fixed alkali hydroxide or when it is passed through a U tube filled with solid KOH or soda lime (distinction and separation from As). Alkali carbonates and alkaline earth hydroxides also decompose SbH_3.[4]

When SbH_3 is passed into a solution of $AgNO_3$, the silver is reduced and the Sb converted to the oxide (or acid) which is only slightly soluble in H_2O (distinction from As):[5]

$$SbH_3 + 3\ AgNO_3 = Ag_3Sb + 3\ HNO_3$$

$$Ag_3Sb + 3\ AgNO_3 + 3\ H_2O = 6\ Ag + H_3SbO_3 + 3\ HNO_3$$ [6]

The precipitate should be washed free from excess $AgNO_3$ and H_3AsO_3 if present, then treated with dilute HCl (tartaric acid may be used in place of HCl) which dissolves the antimony and leaves the silver. The filtrate from this operation may be tested for Sb.[7]

Stibine is not evolved by the action of Zn or Al and NaOH nor by sodium-amalgam in neutral or alkaline solution (distinction from As^{+3}); the antimony is precipitated as the metal.[8] Stibine is slowly oxidized by

[1] For comparison with arsine and details of manipulation see: §69, 6′, *a*; also Rüdisüle, I, 200 *et seq.*

[2] Stock and Doht, *Ber.*, **34**, 2339, 3592 (1901); **35**, 2270 (1902).

[3] Gaseous SbH_3 explodes if heated to 200° unless diluted with 75% or more of hydrogen.

[4] Stock and Guttmann, *Ber.*, **37**, 885 (1904).

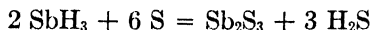
[5] For many methods distinguishing between AsH_3 and SbH_3 see Rüdisüle, I, 200 *et seq.*

[6] Reckleben, *Ber.*, **42**, 1458 (1909); Mellor, IX, 399.

[7] Since AgCl is somewhat soluble in HCl enough may be present to interfere with the test for Sb. Therefore it is best to first add a drop or two of KI and remove any AgI formed.

[8] Fleitmann, *J. Ch. Soc.*, **4**, 329 (1852); Gatehouse, *Ch. News*, **27**, 189 (1873).

sulfur to Sb_2S_3 in the sunlight at room temperature and rapidly at 100°:

$$2\ SbH_3 + 6\ S = Sb_2S_3 + 3\ H_2S$$

k. A solution of an antimony salt on being heated with iron wire in the presence of HCl gives a black precipitate of Sb (distinction from Sn). Metallic Zn, Sn or Mg will give the same result as the iron wire. Copper in concentrated HCl (Reinsch's test[1]) becomes coated with a violet deposit if Sb be present. If a drop of solution containing antimony be placed on a silver coin and the coin touched through the drop with a piece of tin or zinc a black spot will form.[2] Sulfides interfere.

7. Ignition. — Antimonic acid or anhydride upon ignition in the absence of reducing agents forms Sb_2O_4. This upon further heating is reduced to Sb_2O_3 (cf. 4, *b*).

The antimonates of the fixed alkali metals are not vaporized or decomposed when ignited in the absence of reducing agents; hence, by fusion with Na_2CO_3 and an oxidizing agent, e.g., $NaNO_3$, the compounds of Sb are converted into non-volatile sodium pyroantimonate, $Na_4Sb_2O_7$, and arsenic compounds if present are at the same time converted into sodium arsenate, Na_3AsO_4. If the fused mass be digested and disintegrated in cold H_2O and filtered, the antimonate remains in the residue as $Na_2H_2Sb_2O_7$ (NaH_2SbO_4) (4, *c*), while the arsenate dissolves. The operation is more satisfactory when the As and Sb are previously fully oxidized — as by digestion with HNO_3 — since the oxidation by fusion is not effected soon enough to prevent some loss of the lower valence compounds by volatilization. If compounds of tin be present and if the fusion temperature be below that required to convert $NaNO_2$ into Na_2O and form the soluble Na_2SnO_3, the Sn will be left as SnO_2 in the residue with $Na_2H_2Sb_2O_7$. If NaOH be added the Sn accompanies the arsenic as Na_2SnO_3.

All compounds of Sb are completely reduced in the dry way on charcoal with Na_2CO_3, more rapidly with KCN, the metal fusing to a globule which if sufficiently pure when cooled will have on its surface a crystalline net work, the so-called "antimony star." The reduced metal rapidly oxidizes, the white Sb_2O_3 rising in fumes, and making a crystalline deposit on the support. If, now, $(NH_4)_2S$ be added to the sublimate, an orange precipitate is proof of the presence of Sb. The same white oxide is formed on heating Sb or its sulfides in a glass tube through which air is allowed to pass.

8. Detection. — Antimony is precipitated from HCl solution in the second group by H_2S as the sulfide. Treated with $(NH_4)_2S_2$ it is separated from Hg, Pb, Bi, Cu and Cd. The filtrate is acidified and digested with hot concentrated HCl whereupon the Sb and Sn are separated from As. Boiling the HCl solution with Fe precipitates metallic antimony which can be identified by means of Marsh's test. A sample of the HCl solution may be tested by means of the Reinsch or the silver coin test,[3] (6, *k*). In absence of arsenic and other interfering substances antimony may be detected by means of the Gutzeit test (§69, 6′, *b*).[4, 5, 6]

[1] Evans, *Analyst*, **48**, 358–67, 417–29 (1923).

[2] This may be considered as a modification of Rideal's iron-platinum couple test, *Ch. News*, **51**, 292 (1885); cf. Haferkorn, *Ch. Ztg.*, **46**, 186 (1922), who confirmed Hoffer's statement, *Ch. Ztg.*, **46**, 186 (1922), that a Hg mirror and Cu wire may be used.

[3] Using the Fe-Pt couple it is claimed that 0.0_412 g. of Sb can be detected.

[4] See also Sabalitschka and Schmidt, *Ber. deut. pharm. Ges.*, **32**, 132 (1922).

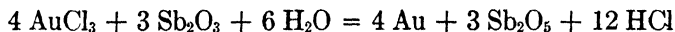
[5] Eegriwe, *Z. anal. Ch.*, **70**, 400–3 (1927), has suggested the use of tetraethylrhodamine for the detection of Sb, claiming a sensitivity to 0.0005 mg. of Sb.

[6] Gutzeit, *Helv. Ch. Acta*, **12**, 713–40 (1929); *C.A.* **23**, 4644, describes a number of tests for Sb.

9. Determination. — *Gravimetrically,* antimony may be separated and weighed (1) as Sb_2S_3.[1] This is probably the most satisfactory method for small amounts of the element. It is however limited in applicability to systems free from Ag, Cu, Bi, As and Sn, i.e., elements forming insoluble sulfides in strongly acid solution. In addition the Sb_2S_3 must be dried in CO_2 at 280–300°. (2) The sulfide may be converted to the oxide and after ignition at about 825° weighed as Sb_2O_4. This modification requires more careful control but otherwise is less troublesome than weighing as the sulfide. *Volumetrically,* antimony is determined by methods similar to those described under arsenic. (§69, 8). (3) Lundell[2] believes that titration of Sb^{+3} with $KMnO_4$ at 5–10° in a solution containing 10%–25% HCl and 10% H_2SO_4 to be the most accurate method for the determination of antimony, if the amount exceeds a few milligrams. (4) Titration of Sb^{+3} with $KBrO_3$ is also a very accurate method. The concentration of HCl must not fall below 20% nor the temperature below 60°. Methyl orange is used as an indicator. (5) Titration in neutral solution (tartrate present) with iodine has also been recommended. (6) For very small amounts of antimony, 0.1 mg. or less, it is probably best to use the modified Gutzeit test and compare the stain produced on $HgBr_2$ with that obtained using known amounts of Sb.[3] (7) Antimony may be determined electrolytically, but in general the above methods are preferred.[4]

10. Oxidation and Reduction. — Stibine, SbH_3, is decomposed by heat alone into Sb and H_2 (6, *j*). By burning in air it is oxidized to Sb_2O_3 and H_2O. Passed into a solution of $AgNO_3$, hydrated Sb_2O_3 is produced, or passed into a solution of $SbCl_3$ or KOH (sp. g. 1.25) metallic antimony is precipitated. With excess of I_2 in presence of water Sb^{+3} is produced; if the stibine be in excess metallic antimony is obtained. Metallic Sb is oxidized by HNO_3, Cl_2, or Br_2, to Sb^{+3} or Sb^{+5}, depending upon the amount of the reagent and the temperature. Iodine oxidizes Sb to Sb^{+3}, in alkaline solutions Sb^{+5} may be formed.

Antimonous compounds are oxidized to antimonic by Cl_2, Br_2, HNO_3, $Cr_2O_7^{--}$ and MnO_4^-; by Ag_2O in presence of the fixed alkalis; by gold chloride in HCl solution, gold being deposited as a yellow precipitate. The Sb is precipitated as Sb_2O_5 unless sufficient acid be present to dissolve the oxide,

$$4\,AuCl_3 + 3\,Sb_2O_3 + 6\,H_2O = 4\,Au + 3\,Sb_2O_5 + 12\,HCl$$

Antimonic compounds are reduced to antimonous by HI and by $SnCl_2$ (distinction from As), NaH_2PO_2 also effects the same change.[5] Sb^{+5} and Sb^{+3} compounds are reduced to the metal by Pb, Sn, Bi, Cu, Cd, Fe, Zn and Mg; but in the presence of dilute acids and metals that evolve hydrogen the reduction is, in part, to SbH_3.

[1] Vortmann and Metzl, *Z. anal. Ch.*, **44**, 525 (1905); Henz, *Z. anorg. allgem. Ch.*, **37**, 1 (1903).

[2] Hillebrand and Lundell, 227–8.

[3] For application of Marsh's test see: Sanger and Gibson, *Z. anorg. allgem. Ch.*, **55**, 205–22 (1907).

[4] For extensive bibliography see: Darling, *Ch. Engr.*, **27**, 11–12, 21, 41–2, 63 (1919); Margosches, Vol. XVI–XVII; Rüdisüle, I, and Nachträge of later volumes.

[5] Evans, *Analyst*, **56**, 171–7 (1931); *C.A.* **25**, 2072.

Sodium amalgam with dilute H_2SO_4 evolves SbH_3 from all antimony compounds but the generation of hydrogen in alkaline solution, e.g., $NaOH + Al$, causes the reduction of antimony to the metal only, no SbH_3 being evolved.

§71. Tin (Anglo-Sax., *tin*) (Stannum) Sn = 118.70. Atomic No. 50. Valence 2 and 4. Discovery prehistoric.

1. Physical Properties. — Density, white, 7.311 at 20°/4°;[1] gray, 5.85 at 15°; commercial, 7.5;[2] melting point, 231.9°;[3] boiling point, 2270° at 755 mm.[4] Tin is a silvery-white metal with a bluish tinge; it does not tarnish readily in pure air. At a red heat it decomposes steam with evolution of hydrogen; heated to near its boiling point it burns in the air with a dazzling white light forming SnO_2. It is softer than zinc, harder than lead, can be hammered or rolled into thin sheets (tinfoil); at 100° it can be drawn into wire and at 200° can be pulverized. The structure of bar or block tin is distinctly crystalline. When a bar is bent a marked creaking or " tin cry " is emitted[5] due to the friction of the crystals. Block tin exposed to low temperatures crumbles to a grayish powder.[6] This " disease," called " tin pest," is contagious. It may be noticed in samples of tin that have been preserved for several hundred years.[7] The explanation of the phenomenon[8] is that the gray form is an allotropic modification, the stable state at lower temperatures. It may be converted back to white tin by heating on a water bath. Tin forms alloys with many metals. Into solder (soft solder is Pb, 50–Sn, 50) goes 20%–25% of the tin used in this country; babbitts (Sn–Sb–Cu) account for 19%, brass (Cu–Zn–Sn–Pb) and bronze (Cu–Sn), 14%. White, type, casting and the easily fusible metals, e.g., Wood's metal, also contain tin.[9]

2. Occurrence. — The chief ore of tin is cassiterite or tinstone, a nearly pure crystallized dioxide, SnO_2. It is obtained chiefly from open mines. The world's production of tin in 1928 amounted to 178,050 tons of which the Federated Malay States furnished 61,955 tons; Bolivia, 41,415 tons and the Dutch East Indies 34,943 tons. The price was 25 cents per pound in 1931.

3. Preparation. — The metallurgy of tin is simple when compared with many of the other important metals and is essentially the same now as it was 2000–4000 years ago. The impure ore is first concentrated by washing and, perhaps, magnetic separation. After roasting to remove sulfur, etc., the concentrate contains 83%–88% SnO_2. This is fused with powdered coal in a reverberatory or blast furnace, lime being introduced to form a fusible slag: $SnO_2 + C = Sn + CO_2$. The crude tin thus obtained may be refined by repeated fusion, by liquation or electrolytically. The " Standard " quality must contain over 99.75% Sn.

4. Oxides and Hydroxides. — Tin forms two stable oxides and corresponding classes of salts. Stannous oxide, SnO, is black or blue-black, and stannic oxide, SnO_2, white. Both act as basic and acidic oxides thus forming four series of compounds, stannous and stannic with acids, stannites and stannates with bases.

Stannous oxide is formed (1) by treating $SnCl_2$ with Na_2CO_3 until the solution reacts

[1] Hoffmann and Stahl, *Metall Erz*, **20**, 5, 41 (1923).
[2] Mantell, "Tin." Chemical Catalog Co. Inc., New York, **1929**, p. 20.
[3] B. Stds. Cir. 35.
[4] Ruff and Bergdahl, *Z. anorg. allgem. Ch.*, **106**, 76 (1919).
[5] Levol, *Ann. ch. phys.*, [3] **56**, 110 (1859).
[6] Erdmann, *J. prakt. Ch.*, [1] **52**, 428 (1851).
Fritzsche, *Mem. Acad. St. Petersburg*, [1] **7**, 15 (1870); *Ber.*, **2**, 112 (1869).
[7] Schertel, *J. prakt. Ch.*, [2] **19**, 322 (1879).
[8] Cohen and van Eijk, *Z. physik. Ch.*, **30**, 601 (1899).
[9] Mantell, *Ibid.*, p. 170–240.

alkaline to phenolphthalein, and digesting at 110° for several hours, whereupon the precipitate becomes black:[1] (2) by ignition of stannous oxalate in an inert atmosphere.

Stannous hydroxide, $Sn(OH)_2$,[2] white, is formed by adding alkalis or alkali carbonates to $SnCl_2$, washing and drying the precipitate at a low temperature.[3] Precipitation starts at *p*H 1.9.[4] The product is gelatinous and slowly absorbs oxygen from the air forming hydrated stannic oxide. Stannous hydroxide is amphoteric forming Sn^{++} with acids and SnO_2^{--} with strong bases. The stannites are powerful reducing agents; they are found only in solution; decompose readily into tin and stannic oxide; absorb oxygen on standing forming stannate and metastannic acid.

Stannic oxide, SnO_2, is found native as tinstone which is nearly pure, crystalline SnO_2. The oxide is prepared (1) by heating tin in the air to a white heat. The finely divided white product was formerly called Flors jovis; it is used to make glazes and enamels opaque. (2) Stannic salts are treated with an alkali carbonate, the precipitate washed and ignited. (3) Tin is oxidized with HNO_3. Artificially prepared SnO_2 differs chemically in many respects from the natural product.

Stannic hydroxide or stannic acid, $SnO_2 \cdot nH_2O$, exists apparently in at least two modifications (Fremy's stannic acid and metastannic acid; Berzelius' α- and β-stannic acid). X-ray pictures of powders of the two forms indicate that they are identical but that the β form has coarser particles.[5] It has also been stated that the α and β acids are hydrous stannic oxides whose composition and properties are determined by the conditions of formation.[6] The α acid is obtained (1) by treating a stannic salt with an alkali, (2) by adding acid to stannates. The white product when dried looks like gelatin; moistened, it turns blue litmus red; treated with alkalis it reacts as a dibasic acid, forming $Na_2SnO_3 \cdot 3H_2O$; heated, it rapidly changes to the β form. β-stannic acid is also obtained when tin is oxidized with HNO_3.[7] It is said to be less acid than the α modification, forming stannates ($M_2Sn_5O_{11} \cdot 4H_2O$) when treated with dilute alkalis. The formula $H_{10}Sn_5O_{15}$, i.e., $(H_2SnO_3)_5$, was formerly given for β-stannic acid. As would be expected $Sn(OH)_4$ is a stronger acid than base while $Sn(OH)_2$ is a stronger base than acid, hence many stannates have been described in the literature. The composition (and existence) of some of them is doubtful and that of others varies with the mode of preparation. In general the formula is $M_2Sn(OH)_6 \cdot nH_2O$ where M is a univalent metal.[8]

5. Solubilities. — *a. Metal.* — Tin dissolves in HCl slowly when the acid is cold and dilute, but rapidly when hot and concentrated,[9] $SnCl_2$ and H_2 being produced (Eq. 1); readily dissolved in hot HBr and HI; attacked by alkaline hypochlorites; dissolved by $HClO_3$ with formation of $SnCl_4$[10] (Eq. 2); in dilute H_2SO_4, slowly, with liberation of H_2 (Eq. 3), the acid must be more concentrated than $H_2SO_4 \cdot 6H_2O$;[11] in hot concentrated H_2SO_4 rapidly, with liberation of SO_2 and S (Eq. 4); HNO_3 rapidly con-

[1] Ditte, *Ann. ch. phys.*, [5] **27**, 145 (1882); Fraenkel and Snipischsky, *Z. anorg. allgem. Ch.*, **125**, 235 (1922).

[2] Bury and Partington, *J. Ch. Soc.*, **121**, 1998–2004 (1922), suggest $3SnO \cdot 2H_2O$.

[3] Ditte, *loc. cit.*

[4] Britton, *J. Ch. Soc.*, **127**, 2110 (1925).

[5] Posnjak, *J. Phys. Ch.*, **30**, 1073–7 (1926); Yamada, *J. Ch. Soc. Japan*, **44**, 210–9 (1923); cf. Mecklenberg, *Z. anorg. allgem. Ch.*, **74**, 207–80 (1912); Gutbier *et al.*, *Ber.*, **59B**, 1232–46 (1926).

[6] Weiser, *J. Phys. Ch.*, **26**, 654–86 (1922); cf. Pascal, *Compt. rend.*, **175**, 1063–5 (1922).

Ghosh, *J. Ch. Soc.*, **1928**, 3027–38; *C.A.* **23**, 1332, states regarding the interaction of acids and neutral salts with SnO_2 that the adsorption theory offers a better explanation for the observed facts than the chemical theory of insoluble salt formation.

[7] Cf. Engel, *Compt. rend.*, **124**, 765 (1897); **125**, 464, 651, 709 (1897), who states that the nature of the product depends upon the acid concentration.

[8] Cf. Mantell, *Ibid.*, p. 273 *et seq.*

[9] Centnerszwer, *Z. physik. Ch.*, **A141**, 167–79 (1929); *C.A.* **23**, 5084, says that with the exception of HNO_3 tin is indifferent to strong mineral acids and that the solubility in HCl is effected only when [HCl] is greater than 6 *N*.

[10] Hendrixson, *J. Am. Ch. Soc.*, **26**, 747 (1904).

[11] Ditte, *Ann. ch. phys.*, [5] **27**, 145 (1882).

verts it into β-stannic acid, insoluble in acids (Eq. 5); dilute HNO_3 dissolves it without evolution of gas as $Sn(NO_3)_2$ and NH_4NO_3 (Eq. 6);[1] nitrohydrochloric acid dissolves tin easily as $SnCl_4$ (Eq. 7); KOH dissolves it very slowly, and by atmospheric oxidation (Eq. 8); or, at high temperatures with the evolution of hydrogen (Eq. 9). The halogens combine with Sn directly forming the corresponding halide; fluorine requires a temperature of about 100° but chlorine and bromine react at room temperature.[2]

(1) $Sn + 2\,HCl = SnCl_2 + H_2$
(2) $6\,Sn + 24\,HClO_3 = SnCl_4 + 5\,Sn(ClO_3)_4 + 12\,H_2O$
(3) $Sn + H_2SO_4 = SnSO_4 + H_2$
(4) $Sn + 2\,H_2SO_4 = SnSO_4 + 2\,H_2O + SO_2$
$2\,SnSO_4 + SO_2 + 2\,H_2SO_4 = 2\,Sn(SO_4)_2 + S + 2\,H_2O$
(5) $15\,Sn + 20\,HNO_3 + 5\,H_2O = 3\,H_{10}Sn_5O_{15} + 20\,NO$
(6) $4\,Sn + 10\,HNO_3 = 4\,Sn(NO_3)_2 + 3\,H_2O + NH_4NO_3$
(7) $Sn + 2\,Cl_2$ (aqua regia) $= SnCl_4$
(8) $2\,Sn + 4\,KOH + O_2 = 2\,K_2SnO_2 + 2\,H_2O$
(9) $Sn + 2\,KOH = K_2SnO_2 + H_2$

b. Oxides. — Stannous oxide is insoluble in H_2O, soluble in acids,[3] oxidized by HNO_3 when heated, forming the insoluble β-stannic acid. Stannous hydroxide is readily soluble in all the solvents of the oxide, and is also readily soluble in fixed alkali hydroxides. Stannic oxide is insoluble in H_2O; difficultly soluble in alkalis; insoluble in acids except concentrated H_2SO_4. Sulfur forms SnS_2 and SO_2; fusion with sulfur and Na_2CO_3 gives sodium thiostannate (a common analytical procedure). Freshly precipitated α-stannic acid is soluble[4] in fixed alkali hydroxides and in acids;[5] insoluble in H_2O and changed by hot HNO_3 to the insoluble β-stannic acid. β-stannic acid is insoluble in water and acids, HCl changes it to soluble $Sn_5O_5Cl_2(OH)_8$(?) which upon further addition of acid becomes insoluble $Sn_5O_5Cl_4(OH)_6$(?);[6] soluble in the fixed alkalis forming stannates that are soluble in H_2O and precipitated by acids; insoluble in Na_2CO_3 or NH_4OH. β-stannic acid in contact with HCl is gradually changed to the α form.

c. Salts. — The sulfides and phosphates of tin are insoluble in water, also stannous oxychloride; $SnSO_4$,[7] $SnBr_2$, SnI_2, $SnCl_4$, and $SnBr_4$ dissolve in pure water with little or no decomposition.[8] $SnCl_2$ is soluble in less than two parts of H_2O,[9] but more decomposes it unless excess acid be present ($2\,SnCl_2 + H_2O = SnO{\cdot}SnCl_2 + 2\,HCl$). A small amount of H_2O added to pure, liquid $SnCl_4$ combines exothermically to form crystals of $SnCl_4{\cdot}3H_2O$, readily soluble in excess H_2O; not readily decomposed by boiling H_2O. The nitrates of tin are very easily decomposed by H_2O and require free acid to keep them in solution.[10] SnI_4 is readily soluble in

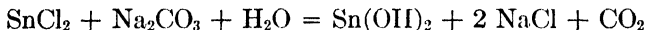
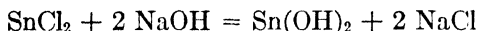
[1] Cf. Engel, *loc. cit.*; Maumene, *Bull. soc. ch.*, [2] **35**, 598 (1881); Gmelin-Kraut, 7th ed., IV, pp. 253–4.
[2] Carnelly and O'Shea, *J. Ch. Soc.*, **33**, 55 (1878).
[3] Ditte, *loc. cit.*
[4] That is, "peptized" from the standpoint of colloid chemistry.
Cf. Weiser, "The Hydrous Oxides," McGraw-Hill Book Co. Inc., New York, **1926**.
[5] Ditte, *Compt. rend.*, **104**, 172 (1887).
[6] Treadwell, "Kurzes Lehrbuch der analytischen Chemie," F. Deuticke, Leipzig und Wien, **1908**, Vol. I, p. 215.
[7] See, however, Ditte, *Ann. ch. phys.*, [5] **27**, 161 (1882).
[8] Carnelley and O'Shea, *J. Ch. Soc.*, **33**, 55 (1878).
[9] Engel, *Ann. ch. phys.*, [6] **17**, 347 (1891).
[10] Montemartini, *Gazz. ch. ital.*, **22**, 384 (1892).

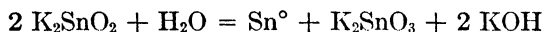
H_2O.[1] $Sn(SO_4)_2$ is easily soluble in H_2O, but is decomposed by a large excess.[2] $SnCl_2$, $SnCl_4$, and SnI_4 are soluble in ethanol; $Sn(NO_3)_2$, $Sn(SO_4)_2$ and $SnBr_4$ are deliquescent. SnS is insoluble in H_2O, soluble in HCl with evolution of H_2S; decomposed by HNO_3 with oxidation to β-stannic acid; insoluble in solution of the normal alkali sulfides; soluble in the polysulfides with oxidation to a stannic compound (6, *e*); decomposed by strong caustic solutions forming tin, alkali stannates and thiostannates.[3] SnS_2 is soluble in HCl with liberation of H_2S; and in solutions of the alkali sulfides. Stannous oxalate is soluble in acids.

6. Reactions.[4] — *a.* Alkali hydroxides and carbonates[5] precipitate from solutions of Sn^{++}, stannous hydroxide, $Sn(OH)_2$ (cf. 4), white, readily soluble in excess of the fixed alkali hydroxides, insoluble in H_2O, NH_4OH and the alkali carbonates (distinction from Sb). It is also precipitated by $BaCO_3$ in the cold:

$$SnCl_2 + 2\ NaOH = Sn(OH)_2 + 2\ NaCl$$

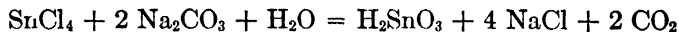
$$SnCl_2 + 4\ NaOH = Na_2SnO_2 + 2\ NaCl + 2\ H_2O$$

$$SnCl_2 + Na_2CO_3 + H_2O = Sn(OH)_2 + 2\ NaCl + CO_2$$

Upon heating a solution of alkali stannite, black crystalline stannous oxide, SnO, is formed. When rapidly boiling a concentrated KOH solution of stannite, part of the tin is oxidized and the remainder precipitated as metallic tin:

$$2\ K_2SnO_2 + H_2O = Sn^\circ + K_2SnO_3 + 2\ KOH$$

The reaction proceeds more rapidly upon addition of a little tartaric acid. $Bi(NO_3)_3$ added to a solution of Na_2SnO_2 gives a black precipitate of metallic bismuth.[6] Sn^{+4} is precipitated by alkali hydroxides and carbonates as stannic acid (cf. 4) soluble in excess of the fixed alkali hydroxides, insoluble in NH_4OH and the alkali carbonates.[7]

$$SnCl_4 + 4\ KOH = H_2SnO_3 + 4\ KCl + H_2O$$

$$SnCl_4 + 6\ KOH = K_2SnO_3 + 4\ KCl + 3\ H_2O$$

$$SnCl_4 + 2\ Na_2CO_3 + H_2O = H_2SnO_3 + 4\ NaCl + 2\ CO_2$$

[1] Schneider, *Pogg. Ann.*, **127**, 624 (1866).
[2] Ditte, *Compt. rend.*, **104**, 172 (1887).
[3] Cf. Perkin, *J. Soc. Ch. Ind.*, **20**, 425 (1901).
[4] For a recent extensive bibliography on compounds of tin see Fehling, X, 490–540, for approximately 750 references.
[5] Although carbonates of tin are mentioned in the literature, their existence is questioned.
[6] Vanino and Treubert, *Ber.*, **31**, 1113 (1898).
[7] Ditte, *Ann. ch. phys.*, [6] **30**, 282 (1893); cf. Mecklenburg, *Z. anorg. allgem. Ch.*, **64**, 368 (1909); **74**, 207 (1912); **84**, 121 (1914).

β-stannic salts yield a precipitate of β-stannic acid, soluble in KOH not too concentrated; an excess precipitates potassium β-stannate, soluble in water; not readily soluble in NaOH; insoluble in NH_4OH and the alkali carbonates. Tartaric acid prevents the precipitation of $Sn(OH)_2$ by alkali hydroxides and carbonates; similarly stannic chloride gives no precipitate but the action of β-stannic chloride is unaffected.

b. Oxalic acid forms a white crystalline precipitate of SnC_2O_4 with a nearly neutral solution of $SnCl_2$; soluble in HCl; NH_4Cl prevents the precipitation. If a nearly neutral solution of $SnCl_2$ be added dropwise to a solution of $(NH_4)_2C_2O_4$, the white precipitate formed at once dissolves in the excess of reagent. $SnCl_4$ gives no precipitate with oxalates.

Potassium cyanide precipitates both $Sn(CN)_2$ and $Sn(CN)_4$, white, insoluble in excess of the cyanide. $K_4Fe(CN)_6$ precipitates, from $SnCl_2$ solutions, stannous ferrocyanide, $Sn_2Fe(CN)_6$, white, insoluble in H_2O, soluble in hot, concentrated HCl. $SnCl_4$ gives a greenish white, gelatinous precipitate soluble in hot, concentrated HCl, but reprecipitated upon cooling (distinction from Sb).[1] $K_3Fe(CN)_6$ precipitates from solutions of $SnCl_2$ stannous ferricyanide, $Sn_3[Fe(CN)_6]_2$, white, readily soluble in HCl. On warming, the ferricyanide is reduced to ferrocyanide with oxidation of the tin. No precipitate is formed by $Fe(CN)_6^{-3}$ with $SnCl_4$.

c. The nitrates of tin are not stable. Stannous nitrate is deliquescent and soon decomposes on standing exposed to the air. Stannous salts when heated with HNO_3 yield a precipitate of β-stannic acid; $SnCl_2$ warmed with a mixture of equal parts of HCl and HNO_3 forms stannic chloride and ammonium ion: $8\ SnCl_2 + 18\ HCl + 2\ HNO_3 = 7\ SnCl_4 + (NH_4)_2SnCl_6 + 6\ H_2O$. With HCl absent the reaction is: $6\ SnCl_2 + 4\ HNO_3 = 3\ SnCl_4 + 3\ SnO_2 + 4\ NO + 2\ H_2O$.[2]

d. Hypophosphorous acid does not form a precipitate with Sn^{++} or Sn^{+4} nor are these ions reduced when boiled with the acid. Sodium hypophosphite produces a white precipitate when added to $SnCl_2$, soluble in excess of HCl; no precipitate is formed with $SnCl_4$. Phosphoric acid and soluble phosphates precipitate from Sn^{++} solutions, not too strongly acid, stannous phosphate,[3] white, composition variable, soluble in various acids and KOH, insoluble in H_2O.[4] A white gelatinous precipitate is formed with $SnCl_4$, soluble in HCl and KOH, insoluble in HNO_3 and $HC_2H_3O_2$. If the $SnCl_4$ be dissolved in excess NaOH before the addition of Na_2HPO_4 and the mixture then acidified with HNO_3, the tin is completely precipitated as stannic phosphate (separation from Sb). However,

[1] Wyrouboff, *Ann. ch. phys.*, [5] **8**, 458 (1876).
[2] Scheurer-Kestner, *Ann. ch. phys.*, [3] **58**, 471 (1860); *Compt. rend.*, **50**, 50–2 (1860); Mellor, VII, 430.
[3] Jabłczyński and Więckowski, *Z. anorg. allgem. Ch.*, **152**, 207 (1926).
[4] Lenssen, *Ann.*, **114**, 113 (1860).

the precipitate always is contaminated with a little Sb.[1] Stannous and stannic meta- and pyrophosphates have been prepared.[2]

e. Hydrosulfic acid and soluble sulfides precipitate, from neutral or acid[3] solutions of Sn^{++}, dark brown, hydrated (?) stannous sulfide, SnS (Eq. 1),[4] insoluble in dilute, soluble in moderately concentrated HCl (Eq. 2). It is readily dissolved with oxidation by alkali polysulfides, forming thiostannates (Eq. 3), from which acids precipitate the yellow SnS_2 (Eq. 4). The normal, alkali sulfides scarcely dissolve any SnS at room temperature (cf. § 69, 6, *e* and §70, 6, *e*), but concentrated K_2S dissolves SnS forming K_2SnS_3 and Sn (Eq. 5).[5] Potassium and sodium hydroxides dissolve it forming stannite and thiostannite (Eq. 6), from which acids reprecipitate SnS (Eq. 7). Alkali carbonates and NH_4OH do not dissolve it (distinction from As) (distinction from Sb in so far as the reaction with CO_3^{--} is concerned). Nitrohydrochloric acid, i.e., free chlorine, dissolves it forming $SnCl_4$ and S (Eq. 8). HNO_3 converts it to β-stannic acid (Eq. 9) (separation from As[6]). H_2O_2 in alkaline solution oxidizes it to thiostannate and stannate (Eq. 10). Heated with $CuSO_4$ or $CdSO_4$ it is converted to $SnSO_4$. Fused with KCN metallic tin is obtained.

(1) $SnCl_2 + H_2S = SnS + 2\ HCl$

(2) $SnS + 2\ HCl = SnCl_2 + H_2S$

(3) $SnS + (NH_4)_2S_2 = (NH_4)_2SnS_3$

(4) $(NH_4)_2SnS_3 + 2\ HCl = SnS_2 + 2\ NH_4Cl + H_2S$

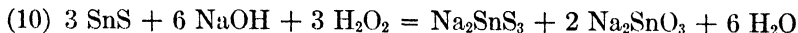
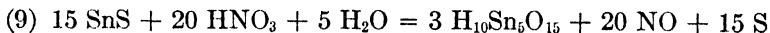
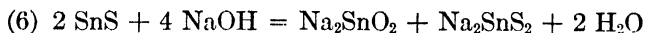
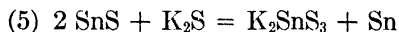
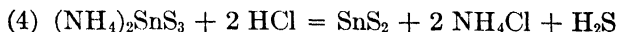
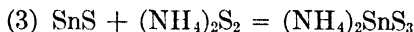
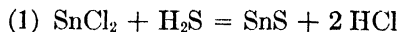
(5) $2\ SnS + K_2S = K_2SnS_3 + Sn$

(6) $2\ SnS + 4\ NaOH = Na_2SnO_2 + Na_2SnS_2 + 2\ H_2O$

(7) $Na_2SnO_2 + Na_2SnS_2 + 4\ HCl = 2\ SnS + 4\ NaCl + 2\ H_2O$

(8) $SnS + 2\ Cl_2 = SnCl_4 + S$

(9) $15\ SnS + 20\ HNO_3 + 5\ H_2O = 3\ H_{10}Sn_5O_{15} + 20\ NO + 15\ S$

(10) $3\ SnS + 6\ NaOH + 3\ H_2O_2 = Na_2SnS_3 + 2\ Na_2SnO_3 + 6\ H_2O$

Sn^{+4} is precipitated as stannic sulfide, SnS_2, yellow, having generally the same solubilities as SnS except that SnS_2 is moderately soluble in normal alkali sulfides. The following equations illustrate the more important reactions:

[1] Bornemann, *Z. angew. Ch.*, **12**, 635 (1899).

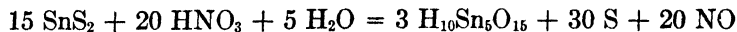
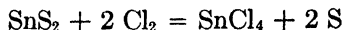
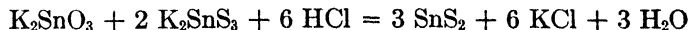
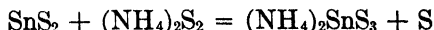
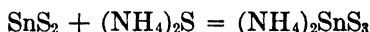
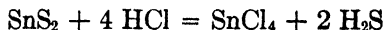
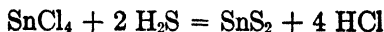
[2] Mellor, VII, 482.

[3] Dede and Bonin, *Ber.*, **55B**, 2327 (1922) give data on effect of H^+ and Cl^- on precipitation of PbS. These may be applied to Sn without serious error.

[4] Precipitation is prevented by $H_2C_2O_4$ or NH_4Cl.

[5] Ditte, *Compt. rend.*, **94**, 1419 (1882); Baubigny, *J. Ch. Soc.*, **44**, 22 (1883).

[6] The separation is poor because the precipitate adsorbs AsO_4^{-3}, also iron, etc.

$$SnCl_4 + 2\,H_2S = SnS_2 + 4\,HCl$$
$$SnS_2 + 4\,HCl = SnCl_4 + 2\,H_2S$$
$$SnS_2 + (NH_4)_2S = (NH_4)_2SnS_3$$
$$SnS_2 + (NH_4)_2S_2 = (NH_4)_2SnS_3 + S$$
$$3\,SnS_2 + 6\,KOH = K_2SnO_3 + 2\,K_2SnS_3 + 3\,H_2O$$
$$K_2SnO_3 + 2\,K_2SnS_3 + 6\,HCl = 3\,SnS_2 + 6\,KCl + 3\,H_2O$$
$$SnS_2 + 2\,Cl_2 = SnCl_4 + 2\,S$$
$$15\,SnS_2 + 20\,HNO_3 + 5\,H_2O = 3\,H_{10}Sn_5O_{15} + 30\,S + 20\,NO$$

SnS_2 is not precipitated by H_2S from a solution containing (1) excess OH^-; (2) excess HCl; (3) the tin as a complex ion, e.g., from $H_2C_2O_4$ solution (distinction from Sb and As), or from HF solution (distinction from Sn^{++}[1] and Sb^{+++}[2]); (4) excess H_3PO_4 (distinction from Sn^{++} and Sb^{+++}).[3]

Ammonium thioacetate precipitates the corresponding sulfide from HCl solutions of Sn^{++} and Sn^{+4}. Sodium thiosulfate does not form a precipitate with Sn^{++}, but SO_2 is liberated from the reagent and oxidizes the Sn^{++} to Sn^{+4} ($SO_2 + 3\,SnCl_2 + 6\,HCl = 3\,SnCl_4 + H_2S + 2\,H_2O$). The H_2S may or may not precipitate SnS_2($6\,SnCl_2 + 2\,SO_2 + 8\,HCl = 5\,SnCl_4 + SnS_2 + 4\,H_2O$);[4] excess reagent will react with the $SnCl_4$ producing a white precipitate of stannic sulfide and hydroxide.[5] Sulfurous acid and sulfites react with Sn^{++} as indicated above. According to Durrant, Sn^{+4} may be reduced to a slight extent, $SnCl_4 + H_2SO_3 + H_2O = SnCl_2 + H_2SO_4 + 2\,HCl$. The sulfates of tin are formed by dissolving the freshly precipitated hydroxides in H_2SO_4 and evaporating at a gentle heat; at higher temperatures (130–200°) $SnSO_4$ is oxidized to $Sn(SO_4)_2$: $SnSO_4 + 2\,H_2SO_4 = Sn(SO_4)_2 + 2\,H_2O + SO_2$.[6] The sulfates are readily decomposed by H_2O.

f. Potassium iodide, added to a concentrated aqueous solution of $SnCl_2$, forms first a yellow precipitate soluble in excess of the $SnCl_2$. Further addition of KI gives a yellow precipitate (rapidly turning to dark orange) of needle-like crystals, often forming rosettes. If a drop of $SnCl_2$ be added to an excess of KI the yellow precipitate is formed, which remains unless more $SnCl_2$ is added, whereupon the orange modification appears. The orange precipitate is probably SnI_2; it is soluble in HCl, KOH, and ethanol, sparingly soluble in H_2O with some decomposition. The yellow product may be a double salt of SnI_2 and KI; it has about the same solubilities as

[1] Fischer and Thiele, *Z. anorg. allgem. Ch.*, **67**, 302 (1910).
[2] McCay and Thiele, *Z. anal. Ch.*, **51**, 680, 682 (1912).
[3] Vortmann and Metzl, *Ibid.*, **44**, 532 (1905).
[4] Fink and Mantell, *J. Phys. Ch.*, **32**, 103–112 (1928).
[5] Donath, *Z. anal. Ch.*, **36**, 663 (1897); Durrant, *J. Ch. Soc.*, **107**, 622 (1915).
[6] Durrant, *loc. cit.*

the orange precipitate.[1] KI in concentrated solution precipitates SnI_4, yellow, from very concentrated aqueous solutions of $SnCl_4$. The precipitate is readily soluble in H_2O and HCl giving a colorless solution.[2] HI does not give I_2 with Sn^{+4} (distinction from Sb^{+5} and As^{+5}).[3]

Stannous hydroxide, freshly prepared, dissolves in $HClO_3$ forming stannous chlorate which quickly decomposes explosively.[4] Brönner[5] found that $KClO_3$ rapidly oxidizes Sn^{++} to Sn^{+4}. $KBrO_3$ and KIO_3 react with Sn^{++} forming yellowish to white salts that quickly decompose liberating Br_2 and I_2 respectively.[6] $KClO_3$, $KBrO_3$ and KIO_3 all form precipitates with $SnCl_4$, soluble in HCl without liberation of halogen.[7]

g. When an alkali arsenite is added to a solution of $SnCl_2$ a white precipitate of stannous arsenite is obtained, $3\ SnCl_2 + Na_4As_2O_5 + H_2O = Sn_3(AsO_3)_2 + 4\ NaCl + 2\ HCl$.[8] The precipitate decomposes upon heating. Added to $SnCl_4$, the arsenite precipitates stannic orthoarsenite, white, which also decomposes upon heating. Stannous arsenate, $SnHAsO_4 \cdot \frac{1}{2}H_2O$, a voluminous flocculent precipitate, is formed by adding a solution of $SnCl_2$ to an acetic acid solution of AsO_4^{-3}.[9] It also decomposes upon heating to As, As_2O_3 and SnO_2. Stannic arsenate, $2SnO_2 \cdot As_2O_5 \cdot 10H_2O$, a gelatinous white precipitate, is obtained upon adding HNO_3 to a mixture of Na_2SnO_3 and Na_3AsO_4.[10] With antimony, tin acts as a base, forming stannous and stannic antimonites and antimonates.[11]

h. If K_2CrO_4 is added to an HCl solution of $SnCl_2$ there is an immediate reduction of the Cr^{+6} to Cr^{+3}. If $SnCl_2$ is carefully added to K_2CrO_4 in excess, an abundant yellow precipitate is obtained without much apparent reduction of the chromium.[12] K_2CrO_4 added to $SnCl_4$ gives a bright yellow precipitate, soluble in excess of $SnCl_4$, insoluble in H_2O, difficultly soluble in HCl. $K_2Cr_2O_7$ also gives a precipitate with $SnCl_2$ and $SnCl_4$.[13]

i. A solution of $Ag(NH_3)_2NO_3$ reacts with SnO_2^{--} to give metallic sil-

[1] Personne, *Compt. rend.*, **54**, 216 (1862); Heller, *Z. anal. Ch.*, **61**, 180 (1922).

[2] Schneider, *Pogg. Ann.*, **127**, 624 (1866); Bressanin, *Gazz. ch. ital.*, **42**, II, 97–101 (1912); Heller, *loc. cit.*; Mazuir, *Ann. ch. anal. ch. appl.*, [2] **2**, 9 (1920).

[3] Herroun, *J. Ch. Soc.*, **42**, 661 (1882).

[4] Wächter, *J. prakt. Ch.*, **30**, 326 (1843).

[5] Brönner, *Dingler's poly. J.*, **186**, 131 (1867).

[6] Simon, *Repertorium für die Pharmacie*, **65**, 207 (1839).
Rammelsberg, *Pogg. Ann.*, **44**, 567 (1838).

[7] Cf. Ray and Ray, *Quarterly J. Indian Ch. Soc.*, **3**, 110 (1926); Moody, *Am. J. Sci.*, [4] **22**, 176 (1906).

[8] Reichard, *Ber.*, **27**, 1019 (1894); **30**, 1915 (1897); **31**, 2168 (1898). Stavenhagen, *J. prakt. Ch.*, [2] **51**, 32 (1895).

[9] Lenssen, *Ann.*, **114**, 113 (1860).

[10] Haeffely, *Phil. Mag.*, [4] **10**, 290 (1855).

[11] Lenssen, *loc. cit.*; Schiff, *Ann.*, **120**, 55 (1861).

[12] This product has been recommended as a catalyzer in the contact process for making H_2SO_4 (Ellis, U. S. Pat. 1,227,044).

[13] Leykauf, *J. prakt. Ch.*, **19**, 127 (1840).

ver (a delicate test for SnO_2^{--}). The addition of NaOH in excess to an unknown solution removes all heavy metals except those having amphoteric hydroxides (Pb, Sb, As, Sn, Al, Cr, Zn); of these tin only precipitates metallic silver from the strongly ammoniacal solution in the cold. Antimonous and arsenious compounds give the black precipitate of metallic silver if the solution be boiled.

j. A solution of $HgCl_2$ reacts with $SnCl_2$ forming $SnCl_4$ and a precipitate of Hg_2Cl_2, white, or Hg°, gray, or a mixture of the two, depending upon the temperature and relative amount of reagent (§58, 6, *g*).

k. Stannous salts react with $(NH_4)_2MoO_4$ giving a blue colored solution of the lower valences of Mo. The color varies with the concentration and acidity of the solution (Sb, if present, gives a green color). Using a freshly prepared reagent one part of Sn in 1.5 million may be detected.[1] The test has been modified by Canancio who recommends the addition of CNS^- to the molybdate in HCl solution. A red color is obtained upon addition of Sn^{++}.[2]

7. Ignition. — Before the blowpipe, on charcoal, with Na_2CO_3 and more readily by addition of KCN, tin is reduced to malleable lustrous globules, sometimes rather minute. A little of the white incrustation of SnO_2 will collect on the charcoal near the mass, and, by persistence of the flame on the globules, the same coating forms upon them. SnO_2 ignited with carbon or fused with KCN gives metallic tin.

8. Detection. — Tin is precipitated, by H_2S in the second group, as SnS or SnS_2 (6, *e*) from a solution acidified with HCl (0.25 *N*). It is separated from the copper division (Hg, Pb, Bi, Cu and Cd) by solution in $(NH_4)_2S_x$, giving in either case $(NH_4)_2SnS_3$, ammonium thiostannate. This solution, treated with HCl, forms SnS_2 which dissolves in more concentrated acid as $SnCl_4$ (separation from As). After filtration the addition of powdered iron[3] reduces the tin to Sn^{++} (Sb is precipitated as the metal) which may be detected by means of $HgCl_2$ (6, *j*), $(NH_4)_2MoO_4$ (6, *k*), KI (6, *f*), $Bi(NO_3)_3$ (6, *a*), etc.[4]

Reichard has suggested a test for Sn based upon the formation of a black precipitate when $SnCl_4$ is treated with alkaline uric acid.[5]

9. Determination. — *Gravimetrically*, tin is (1) converted to SnO_2 and weighed; (2) deposited electrolytically from either oxalic acid or thiostannate solution and weighed as metallic tin.[6] *Volumetrically*, tin may be determined, after reduction to Sn^{++}, by

[1] Hüttig, *Ch. Ztg.*, **47**, 341–2 (1923); Feigl, *Ibid.*, **47**, 561 (1923); Longstaff, *J. Am. Ch. Soc.*, **22**, 450 (1900); Denigés, *J. pharm. ch.* [5] **30**, 207 (1894).

[2] Canancio, *Anales soc. españ. fís. quím.*, **9**, 177–8 (1911); *C.A.* **5**, 3211; cf. Guzmán, *Ch. Ztg.*, **35**, 797 (1911).

[3] The use of Al in place of Fe is recommended by Scott and Koelsche, *J. Ch. Ed.*, **7**, 367–8 (1930); *C.A.* **24**, 1314.

[4] Cf. Fehling, X, pp. 441–6.

[5] Reichard, *Pharm. Zentralhalle*, **47**, 391 (1906).

[6] Cf. Baxter and Starkweather, *J. Am. Ch. Soc.*, **42**, 905 (1920); Brauner and Krepelka, *Ibid.*, p. 917.

titration with (1) standard iodine in an atmosphere of CO_2 using starch as an indicator; (2) standard $FeCl_3$ under the conditions just stated using molybdic acid to determine the end point;[1] (3) standard KIO_3, the $SnCl_2$ having at least 10% HCl present. Chloroform or CCl_4, giving a violet color with iodine, is used as an indicator.[2]

10. Oxidation and Reduction. — Metallic tin reduces ions of Ag, Hg, Bi, Cu, Pt and Au, to the metallic state. Sn^{++} is oxidized to Sn^{+4} by HNO_2, HNO_3, $H_3Fe(CN)_6$, H_2SO_3, H_2SO_4 (hot), Cl_2, HClO, $HClO_2$, $HClO_3$, Br_2, $HBrO_3$, I_2, HIO_3, $K_2S_2O_8$, PbO_2^{--}, AsO_3^{-3}, and AsO_4^{-3} (in excess HCl), Sb^{+5}, Mo^{+6}, Bi^{+3} (solution alkaline), Cu_2^{++}, Pd^{++}, Pt^{+4}, Fe^{+3}, Cr^{+6}, Co^{+3}, Ni^{+3}, and $Mn^{+3 \text{ to } +7}$. Cl_2, Br_2 and I_2 react more vigorously in alkaline than in acid solution. Excepting bismuth, the metals mentioned at the beginning of this paragraph oxidize Sn^{++} in both acid and alkaline solution.

Stannous chloride is one of the most convenient and efficient of the ordinary discriminative reducing agents for operations in the wet way. Since $SnCl_4$ is soluble in the solvents of $SnCl_2$ no precipitate of tin is obtained as a result of its reducing action, but many other metals do yield precipitates and are thus identified in analysis, e.g., Hg, Ag, As, Bi and Au (forms purple of Cassius).[3]

Solutions of Sn^{+4} are reduced to Sn^{++} by Fe, Ni, Sb, Cu, Pb and Sn. Stannic and stannous salts are reduced to metallic tin by Fe, Cd, Al, Mg, Zn; also by Cu and Pb under certain conditions.

[1] Zengelis, *Ber.*, **34**, 2046 (1901).
[2] Jamieson, *Ind. Eng. Ch.*, **8**, 500 (1916).
[3] Muller, *J. prakt. Ch.*, **30**, 252 (1884).

§72. Comparison of Certain Reactions of Arsenic Antimony and Tin.*

	AsO_3^{-3}	AsO_4^{-3}	Sb^{+3}	Sn^{++}	Sn^{+4}
H_2S (in HCl soln.)	$\underline{As_2S_3}$ lemon yellow	n.v.a. (in 0.25 N HCl) $\underline{As_2S_5}$ (in 5 N HCl)	$\underline{Sb_2S_3}$ orange	$\underline{SnS}$ brown black	$\underline{SnS_2}$ yellow
NaOH	n.v.a.	n.v.a.	$\underline{Sb_2O_3}$ white	$\underline{Sn(OH)_2}$ white $\underbrace{Na_2SnO_2}$ colorless	$\underline{SnO(OH)_2}$ white $\underbrace{Na_2SnO_3}$
NH_4OH	n.v.a.	n.v.a.	$\underline{Sb_2O_3}$ white	$\underline{Sn(OH)_2}$ white	$\underline{SnO(OH)_2}$ white
Zn + H_2SO_4	$AsH_3 \uparrow$	$AsH_3 \uparrow$	$SbH_3 \uparrow$	$\underline{Sn^\circ}$ black	$\underbrace{Sn^{++}}$ colorless $\underline{Sn^\circ}$ black
H_2O (dilution of the concentrated nearly neutral soln.)	n.v.a.	n.v.a.	$\underline{SbOCl}$ white	$\underline{Sn_2OCl_2}$ white	$\underline{SnO(OH)_2}$ white
HNO_3 (+ heat)	$\underbrace{H_3AsO_4}$ colorless	n.v.a.	$\underline{H_3SbO_4}$ white	$\underline{(H_2SnO_3)_n}$ white	$\underline{(H_2SnO_3)_n}$ white
HI	n.v.a.	$\underbrace{H_3AsO_3} + \underbrace{I_2}$ brown	$\underline{\underbrace{SbI_3}}$ yellow	$\underline{\underbrace{SnI_2}}$ orange yellow	$\underline{\underbrace{SnI_4}}$ yellow

* Solutions of H_3AsO_3, H_3AsO_4, $SbCl_3$, $SnCl_2$, and $SnCl_4$ may be used.

Notes. — 1. In this table the letters *n.v.a.* mean no visible action; a straight line under the formula indicates that the substance precipitates; a line with up-turned ends, that the substance is in solution; if both are used, the substance does not precipitate from dilute solutions.

2. When two formulas appear in a single square the upper one indicates the first reaction that occurs, the lower one shows the further reaction with excess of reagent.

3. The text should be consulted for further chemical and physical properties of these substances.

§73. Gold (Sanskrit, *jvalita* from *jval*, to shine) (Aurum) Au = 197.2. Atomic No. 79. Valence 1 and 3. Discovery prehistoric, perhaps the earliest known metal.[1]

1. Physical Properties. — Density, 19.3;[2] melting point, 1063°.[3] Gold is a yellow metal, samples from different parts of the world varying slightly in color. The presence of traces of other metals also affects the color. Gold is softer than silver, harder than tin, and possesses but little elasticity or metallic ring. It is probably the most malleable and ductile of all metals; one gram can be drawn into a wire 2000 meters long. The presence of other metals diminishes the ductility. It may be rolled into sheets 0.0001 mm. thick. It vaporizes at a very high temperature. It is a good conductor of electricity, equal to Cu, slightly inferior to Ag. It has a high coefficient of expansion, hence cannot be molded into forms but must be stamped. Due to its softness, pure gold is seldom used, but is " hardened " by alloying with other metals, e.g., Cu, Ag, Ni, Cd, etc. About two-thirds of the world's production of gold is used for coinage or is held in bar form for international trade. The uses for jewelry and other decorative purposes are too well known to require enumeration.

2. Occurrence. — Gold is usually found native but never perfectly pure, being alloyed, always, with silver, copper, or other metals. A purity of 61%–98% is common. It is found as gold dust in alluvial sand, sometimes as nuggets, and occasionally disseminated in veins of quartz. Gold " ore " varies in value. Some, obtained by dredging, can be mined at a profit, though its gold content is only 4¢–5¢ per ton. The Rand ore assays almost $7.00 per ton. Gold is also obtained as a by-product in the refining of other metals, e.g., copper, lead and zinc. In 1928 the world's production of gold amounted to about four hundred million dollars, of which over half came from the Transvaal in South Africa, a quarter from the United States (California, South Dakota, Alaska, Colorado), Canada and Mexico, and the balance chiefly from Russia, Japan and Australia. The price has been standardized at $20.67 per troy ounce.

3. Preparation. — The metallurgy of gold is chiefly a concentration process involving often the separation of less than a gram of metal from a ton of " gangue." The details of mining depend on the location and nature of the deposit. Two common methods are (1) dredging, and (2) washing down the side of a hill with a powerful stream of water. If necessary, the ore is crushed and then run over tables where, due to the difference in density and rate of flow, the gold particles settle out first, and are held either by " riffles," or mercury, or amalgamated copper plates. The gold thus collected is melted and cast into bars. Another method of separation is the cyanide process, in which the ore is leached with a dilute (0.08%) solution of NaCN, air being present: $4\ Au + 8\ NaCN + O_2 + 2\ H_2O = 4\ NaAu(CN)_2 + 4\ NaOH$.[4] The solution is passed through vats containing zinc turnings, where the gold is removed, $2\ NaAu(CN)_2 + 2\ Zn + 4\ NaCN + 2\ H_2O = 2\ Au + 2\ Na_2Zn(CN)_4 + H_2 + 2\ NaOH$; $2\ NaAu(CN)_2 + Zn = 2\ Au + Na_2Zn(CN)_4$.

Impure gold or " bullion " is refined in various ways, depending upon the amount of gold present. Where the gold content is high, chlorine gas may be blown through the molten bullion to form chlorides of silver and the base metals, which are skimmed off leaving pure gold. When the amount of silver is high, electrolytic separation or removal of the silver by solution in H_2SO_4 are common methods.

4. Oxides and Hydroxides. — Gold forms two series of compounds, Au^+ and Au^{+3}.[5] The former are very unstable and the latter decompose readily on heating to only moderate temperatures. Aurous oxide, Au_2O, purple,[6] is obtained by treating a solution of

[1] This distinction may belong to copper.

[2] Davey, *Phys. Rev.*, [2] **25**, 753 (1925).

[3] B. Stds. Cir. 35.

[4] Dixon, *Ch. News*, **76**, 281 (1897).

[5] Bivalent compounds have also been reported.

[6] Fremy, *Ann. ch. phys.*, [3] **31**, 481 (1851), claims that colloidal gold is present. Cf. Pollard, *J. Ch. Soc.*, **1926**, 1347–9; Lunde, *Z. anorg. allgem. Ch.*, **163**, 345–54 (1927).

AuBr with a slight excess of KOH[1] and boiling the resulting system. Heated to above 205° it commences to decompose into the metal and oxygen. Auric hydroxide, $Au(OH)_3$, brown (variable), is formed upon treating $AuCl_3$ with KOH. The product is purified with difficulty. Dried over $CaCl_2$ at 100° it loses water, forming auric oxide, Au_2O_3, dark brown, which decomposes when heated to 250°.

5. Solubilities. — *a. Metal.* — Gold is not tarnished or affected in any way by H_2O or H_2S. Neither HNO_3[2] nor HCl attack it; chlorine, as a gas or in aqueous solution, converts it to auric chloride, $AuCl_3$; bromine water forms $AuBr_3$.[3] When finely divided it dissolves in HI, if aided by O_2 and KI, forming potassium auric iodide, $KAuI_4$: $4\ Au + 12\ HI + 4\ KI + 3\ O_2 = 4\ KAuI_4 + 6\ H_2O$. Cyanides, with air present, dissolve gold (cf. **3**). Warm concentrated H_2SO_4, with the aid of oxidizing agents (MnO_2, PbO_2, $KMnO_4$, etc.), dissolves gold. The finely divided metal is soluble in $K_4Fe(CN)_6$[4] and in an HCl solution of $CuCl_2$.[5]

b. The oxides and hydroxides of gold are insoluble in H_2O and in dilute oxy-acids; soluble in halogen acids, $4\ HCl + Au(OH)_3 = HAuCl_4 + 3\ H_2O$; soluble in the fixed alkalis with formation of AuO^- or AuO_2^-.

c. Salts of the oxy-acids of gold are practically unknown. Aurous salts are decomposed by H_2O, forming Au° and Au^{+3}. Auric chloride is deliquescent; both the chloride and bromide are readily soluble in H_2O. The iodide is decomposed by H_2O, forming AuI. The complex chlorides, bromides, iodides and cyanides are soluble in H_2O. Aurous sulfide, Au_2S, forms a colloidal solution in H_2O; is insoluble in dilute acids, but soluble in alkali polysulfides and cyanides. Auric sulfide, Au_2S_3, is decomposed by H_2O, is insoluble in dilute HCl[6] or HNO_3, but soluble in aqua regia. Aurous cyanide is slightly soluble in water, soluble in NH_4OH, NaOH, $(NH_4)_2S$, $Na_2S_2O_3$ and alkali cyanides.

6. Reactions. — *a.* The fixed alkali hydroxides and carbonates precipitate, from concentrated solutions, aurous or auric hydroxide (AuOH, violet; $Au(OH)_3$, brown), soluble in excess reagent, forming AuO^- and AuO_2^- respectively. Ammonium hydroxide or ammonium carbonate, added to a solution of $AuCl_3$, gives a dirty yellow precipitate of "fulminating gold," $AuN_2H_3 \cdot 3H_2O$,[7] very explosive. Prepared in the presence of a fixed alkali, the sensitivity is markedly increased.

b. Oxalic acid added to a solution of $AuCl_3$, free from HNO_3 and excess of HCl, slowly but completely reduces the gold, which separates in flakes or forms a mirror on the wall of the container, $2\ AuCl_3 + 3\ H_2C_2O_4 = 2\ Au + 6\ CO_2 + 6\ HCl$. (Separation from platinum, palladium, and other second group metals.) Formaldehyde and other aldehydes precipitate gold from acid or alkaline solutions. (Separation from Cu, Sb, Hg, Zn, Pb, Mn, Sn, As and Pt.) Dimethylglyoxime (or diacetyldioxime) precipitates gold from acid solution; hydrazine and hydroxylamine salts give complete precipitation in acid, neutral, or alkaline solution;[8] H_2O_2 causes precipitation in alkaline solution (distinction from Pt and Ir). Auric acetate is obtained when Au_2O_3 is dissolved in acetic acid; decomposition rapidly ensues with the formation of metallic gold. The complex alkali cyanides of gold are readily obtained by treating the oxides with NaCN, Au_2O giving $NaAu(CN)_2$, and Au_2O_3 forming, in the absence of air, $KAu(CN)_4$. The normal cyanides are obtained by careful neutralization of these complexes. AuCN is a stable, pale yellow powder, insoluble in H_2O; $Au(CN)_3$ is colorless and soluble in H_2O. The aqueous solution is unstable when exposed to air. $K_4Fe(CN)_6$ reduces Au^{+3} to Au^+ forming $KAu(CN)_2$;[9] KCNS forms complex thiocyanates of gold.[10]

[1] Krüss, *Ber.*, **19**, 2541 (1886).
[2] Cf. Dewey, *J. Am. Ch. Soc.*, **32**, 318 (1910).
[3] Meyer, *Compt. rend.*, **148**, 347 (1909). For the action of iodine see: *Ibid.*, **139**, 733 (1904).
[4] Beutel, *Z. anorg. allgem. Ch.*, **78**, 154 (1912).
[5] Mylius, *Ibid.*, **70**, 205 (1911).
[6] Gutbier and Dürrwächter, *Ibid.*, **121**, 266 (1922).
[7] Raschig, *Ann.*, **235**, 355 (1886).
[8] Knoevenagel and Ebler, *Ber.*, **35**, 3055 (1902).
[9] Beutel, *Monatsh.*, **31**, 883 (1910); *Z. anorg. allgem. Ch.*, **78**, 152–4 (1912).
[10] Cleve, *J. prakt. Ch.*, **94**, 14 (1865); Kern, *Ch. News*, **33**, 243 (1876).

c. Nitrates of gold are apparently very unstable. Nitrites precipitate the metal, even from dilute solutions. The precipitate may be colloidal.

d. Sodium orthophosphate does not produce a precipitate when added to a solution of $AuCl_3$; the pyrophosphate forms a double salt. Hypophosphorous and phosphorous acids, as well as their salts, precipitate metallic gold.[1]

e. Hydrosulfic acid precipitates, from cold neutral or acid solutions of $AuCl_3$, black gold sulfide, $8\,AuCl_3 + 9\,H_2S + 4\,H_2O = 24\,HCl + H_2SO_4 + 4\,Au_2S_3$.[2] From hot solution the metal is obtained. The sulfide is insoluble in dilute acids, readily soluble in aqua regia and alkali sulfides.[3] Sodium thiosulfate reacts with $AuCl_3$ to form sodium aurothiosulfate, $Na_3Au(S_2O_3)_2 \cdot \frac{1}{2}H_2O$; if the Au^{+3} solution is very dilute a purple color is first formed.[4] Sodium sulfite forms complexes with aurous gold, e.g., $Na_3Au(SO_3)_2 \cdot 1\frac{1}{2}H_2O$.[5] When added to an alkaline solution of $AuCl_3$, sulfur dioxide reduces acid or neutral solutions of $AuCl_3$, $3\,SO_2 + 2\,AuCl_3 + 6\,H_2O = 3\,H_2SO_4 + 6\,HCl + 2\,Au$. Sulfates form very unstable compounds with gold.[6]

f. Au^+ and Au^{+3} readily form complexes with Cl^-,[7] Br^-, and I^-.[8] Potassium iodide, added in small portions to Au^{+3}, gives a yellow precipitate of aurous iodide, AuI, when equivalent quantities are combined. The precipitate is insoluble in H_2O and soluble in excess reagent: $AuCl_3 + 3\,KI = AuI + 3\,KCl + I_2$. Upon gradually adding $AuCl_3$ to KI there is formed first a dark green solution of $KAuI_4$, then a dark green precipitate of AuI_3, very unstable, decomposed by H_2O, changed in the air to AuI. Iodic acid or KIO_3 precipitates, from a solution of $AuCl_3$, auric iodate, $Au(IO_3)_3$, yellow, soluble in large excess of H_2O. Other halogen oxy-acid salts of Au apparently have not been prepared.

g. Stannous chloride, added to a neutral or acid solution of gold chloride, gives a purple precipitate "purple of Cassius," which consists of a mixture of SnO_2 and Au.[9]

7. Ignition. — Many gold compounds are decomposed by light, all by heat. Separation in the dry way may be readily effected by fusion. Pb_3O_4 is generally one of the components of the fusion mixture. During the reaction it is reduced to Pb, which, with the gold, forms a "button" at the bottom of the crucible. Later the Pb is removed by "cupellation."[10]

8. Detection. — Gold in ores[11] is usually detected (and determined) in the dry way by assaying (see above). In the wet way the sample, if not in solution, is digested with aqua regia to dissolve the gold. The excess acid is removed by evaporation and the gold is precipitated by $H_2C_2O_4$ or $FeSO_4$ and identified by its color (see below). If not removed from the original solution, gold is precipitated in Group II by H_2S, dissolved in $(NH_4)_2S_2$, reprecipitated by HCl along with As_2S_5, and separated from the latter by HNO_3.

A large number of reagents[12] have been suggested for the detection of gold, practically all involving its reduction to the colloidal metal, which imparts various colors to the system, depending upon the particle size: (1) the "purple of Cassius" obtained with $SnCl_2$ has been mentioned;[13] (2) $FeSO_4$ may give a brown or black precipitate, depending

[1] Sieverts, *Z. anorg. allgem. Ch.*, **64**, 36 (1909); Lea, *Am. J. Sci.*, [4] **3**, 64 (1897).
[2] Lassaigne, *J. Ch. Méd.*, **8**, 586 (1832); *Ch. Zentr.*, **3**, 914 (1832). Cf. Gutbier and Dürrwächter, *Z. anorg. allgem. Ch.*, **121**, 266 (1922).
[3] Cf. Hofmann and Höchtlen, *Ber.*, **36**, 3090 (1903).
[4] Brunck, *Ann.*, **327**, 250 (1903).
[5] Cf. Rosenheim, *et. al.*, *Z. anorg. allgem. Ch.*, **59**, 198 (1908).
[6] Schottländer, *Ann.*, **217**, 312 (1883).
[7] Diemer, *J. Am. Ch. Soc.*, **35**, 552–9 (1913).
[8] Campbell, *Trans. Faraday Soc.*, **3**, 104–14 (1907).
[9] Huber, *Physik. Z.*, **25**, 45 (1924); *C.A.* **18**, 1622.
See esp.: Gmelin-Kraut, 7th ed., V, 2, pp. 254–60.
[10] For details see a standard work on assaying.
[11] For Au in crude Pt see: Sporcq, *Bull. soc. ch. Belg.*, **38**, 21–4 (1929); *C.A.* **23**, 2389.
[12] Lenher, *J. Am. Ch. Soc.*, **35**, 546–52 (1913).
[13] Sensitive to 1 part Au in 4 million.
Rose, *Z. anal. Ch.*, **41**, 301 (1902). Cf. Sporcq, *loc. cit.*

upon conditions; (3) H_3AsO_4 plus 2–3 drops of $FeCl_3$ plus a small piece of mossy zinc, produces a purple color;[1] (4) *p*-phenylenediamine gives a green color;[2] (5) *m*-phenylenediamine produces a yellow to brown color, the reaction being very delicate;[3] (6) benzidine acetate gives a blue to green color;[4] (7) " tetramethyl base " (tetramethyldiaminodiphenylmethane) gives a purple to pale blue color;[5] (8) *o*-toluidine gives a yellow color.[6]

9. Determination. — Gold is almost always determined in ores by assay methods, i.e., fusion of an " assay ton " (29.166 g.) of the finely ground ore with a suitable flux. The " button " obtained is " cupelled " to remove Pb, the gold " parted " from the other metals, and weighed. In solution, gold may be separated[7] as the metal by use of SO_2, $FeSO_4$, or $H_2C_2O_4$, then ignited and weighed. *Volumetrically*, gold may be determined by adding standard oxalate and titrating the excess with $KMnO_4$.[8] *Electrolytically*, gold may be deposited from an alkali cyanide, sulfide, or thiocyanate solution. The method is seldom used.

10. Oxidation and Reduction. — Gold is reduced to the metallic state by many reagents, among which may be mentioned: light; the elements Pb, Ag, Hg, Sn, As, Sb, Bi, Cu, Pd, Pt, Te, Fe, Al, Co, Ni, Zn, Mg, P; the ions Fe^{++}, Mn^{++}, Sn^{++}, Ti^{+3}, Hg_2^{++}, As^{+3}, Sb^{+3}, Cu_2^{++}, Cr^{+3}, SO_3^{--}, $C_2O_4^{--}$, NO_2^{-}, PO_2^{-3}, PO_3^{-3}, O_2^{--} (i.e. Na_2O_2); the organic compounds formaldehyde, hydrazine, hydroxylamine, diacetyldioxime, *m*- and *p*-phenylenediamine, benzidine, acetylene, sugar, etc.

§74. Platinum (Spanish, *platina* = small silver). Pt = 195.23. Atomic No. 78. Valence 2 and 4. Discovered by Scaliger in 1558.

1. Physical Properties. — Density, 21.51 ± 0.06;[9] melting point, 1771° ± 2°;[10] sensibly volatile at 1300°.[11] Pure platinum is a tin-white metal, softer than Ag, hardened by the presence of other metals, especially iridium, which it frequently contains. It is surpassed in ductility and malleability only by Au and Ag. Platinum black[12] is the finely divided metal, a black powder readily obtained by treating the solution of a platinum salt with an organic reducing agent. Platinum sponge, a gray spongy mass, is made by ignition of $(NH_4)_2PtCl_6$. These finely divided forms of platinum have marked catalytic power; e.g., a stream of H_2 mixed with air ignites when passed over platinum black; H_2 combines with Cl_2; SO_2 unites with O_2 to form SO_3 (the " contact process " for making H_2SO_4); ethanol is oxidized to acetic acid, formic and oxalic acids to CO_2, As^{+3} to As^{+5}, etc. In 1928 the consumption of platinum by industries in the United States was: chemical, 10.68%; electrical, 17.07%; dental, 12.47%; jewelry, 54.77%.[13]

2. Occurrence. — Platinum, like gold, is found native in alluvial sands; a few very rare compounds are known, e.g., $PtAs_2$. The native metal is never pure, being alloyed

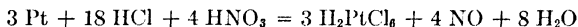
[1] Carnot, *Z. anal. Ch.*, **39**, 191 (1900).
[2] Saul, *Analyst*, **38**, 54 (1913).
[3] Siemssen, *Ch. Ztg.*, **36**, 934 (1912).
[4] Malatesta and Di Nola, *Boll. ch. farm.*, **52**, 461–3 (1913).
[5] Carney, *J. Am. Ch. Soc.*, **34**, 32 (1912).
For a table concerning delicacy of the most important tests for Au see: Vanino and Seeman, *Ber.*, **32**, 1970 (1899); Seeman, Dissert., Erlangen, 1909.
[6] Pollard, *Analyst*, **44**, 94–5 (1919).
[7] Cf. Christensen, *Z. anal. Ch.*, **54**, 158–9 (1915).
[8] Franzeschi, *Z. anal. Ch.*, **41**, 306 (1902).
[9] Davey, *Phys. Rev.*, [2] **25**, 753 (1925).
[10] Hoffmann, *Z. Physik.*, **27**, 285 (1924).
[11] Orcel, *Bull. soc. franc. mineral.*, **49**, 84–5 (1926); *C.A.* **24**, 537.
[12] For platinum black to be used as a catalyst, see, Feulgen, *Ber.*, **54**, 360 (1921).
[13] Mineral Ind., **1929**, p. 490.

with 20%–50% of the other platinum group metals, also Fe, Cu and Au. The world's production is 200,000–300,000 troy ounces, about half of which comes from Russia. Columbia produces one-fourth; South Africa, Canada, and the United States furnish the balance. In the two last named countries, the metal is obtained as a by-product of the refining of Cu, Ni, etc. The price in 1928 averaged $78.58 an ounce, the lowest since 1921.[1]

3. Preparation. — The concentration of platinum from its ores is usually accomplished by washing. The metal is then refined by a wet method. Digestion with aqua regia slowly dissolves the platinum and some of its congeners. The filtrate is treated with lime water until almost neutral, thus precipitating the greater part of the Fe, Cu, Ir, Rh and a portion of the Pd. The filtrate is evaporated to dryness, ignited, and washed with H_2O and HCl. This gives a commercial platinum which may be further purified by a variety of methods.[2] In the laboratory platinum residues are boiled with NaOH or Na_2CO_3 and reduced with alcohol. The fine black powder is filtered, washed with H_2O and HCl, and then ignited.

4. Oxides and Hydroxides. — Platinum forms two important oxides: platinous oxide, PtO, gray or dark violet, and platinic oxide, PtO_2, black. While the corresponding hydroxides, $Pt(OH)_2$ and $Pt(OH)_4$, are described in the literature, it would seem from their reactions that they correspond more nearly to the hydrates, $H_2Pt(OH)_4$ and $H_2Pt(OH)_6$.[3] These compounds are obtained by treating $PtCl_4^{--}$[4] and $PtCl_6^{--}$[5] with NaOH. Gentle heating converts the hydrates to the respective oxides; ignition causes reduction to Pt.

5. Solubilities. — *a. Metal.* — Platinum is not affected by air or H_2O at any temperature; is not sensibly tarnished by H_2S. Fluorine forms PtF_4;[6] Cl_2 forms $PtCl_4$ at a red heat; dry Br_2 and I_2, the halogen acids, HNO_3,[7] and dilute H_2SO_4 have no effect. Hot concentrated H_2SO_4 slowly forms $Pt(SO_4)_2$.[8] Aqua regia, HCl plus $HClO_3$, and HCl containing H_2O_2, dissolve platinum, forming H_2PtCl_6.

$$3\,Pt + 18\,HCl + 4\,HNO_3 = 3\,H_2PtCl_6 + 4\,NO + 8\,H_2O$$

Platinum is attacked upon ignition with alkali nitrates, hydroxides and peroxides, forming platinates.[9] KCN will also dissolve Pt to some extent in the absence of air[10] and presence of H_2O.

b. Oxides and Hydroxides. — Platinous oxide and hydroxide (cf. 4) are soluble in H_2SO_3, but not in the other oxygen acids unless freshly precipitated; soluble in HCl and aqua regia, $Pt(OH)_2 + 4\,HCl = H_2PtCl_4 + 2\,H_2O$, $2\,Pt(OH)_2 = Pt(OH)_4 + Pt$, $Pt(OH)_4 + 6\,HCl = H_2PtCl_6 + 4\,H_2O$. Platinic oxide and hydroxide are soluble in NaOH and acids except acetic.

c. Salts. — Platinum forms two series of salts, platinous and platinic. The oxy-salts are unstable. None of the platinous salts are permanently soluble in H_2O. The chloride is soluble in dilute HCl and the sulfate in dilute H_2SO_4; the nitrate is soluble in

[1] For material on platinum metals see: Lumb, "The Platinum Metals," British Imperial Institute, **1920**. U. S. Geol. Survey, Bull. 694 gives a complete bibliography of the platinum metals to 1918. Cf. Encyclopedie de Chimie Industrielle, Les Métaux Précieux, J. Voisin, **1922**; Ogburn, *J. Ch. Ed.*, **5**, 1371–85 (1928); *C.A.* **23**, 1537. The Russian journal, *Ann. inst. platinc*, has not been easily obtainable in the United States since about 1914.

[2] For details see: Gowland, "The Metallurgy of the Non-ferrous Metals," Charles Griffin and Co., London, **1921**; Wichers, *J. Am. Ch. Soc.*, **43**, 1268 (1921).

[3] Wöhler and Martin, *Ber.*, **42**, 3331 (1909); Gmelin-Kraut, 7th ed., V, 3, p. 248 *et seq.*

[4] Wöhler and Martin, *Z. Elektroch.*, **15**, 792 (1909).

[5] Blondel, *Ann. ch. phys.*, [8] **6**, 103 (1905).

[6] Ruff, *et. al.*, *Ber.*, **46**, 920 (1913).

[7] Pt alloys are not considered here.

[8] Delépine, *Compt. rend.*, **150**, 104 (1910).

[9] Leidié, *Bull. soc. ch.*, [3] **25**, 9 (1901); **27**, 179–83 (1902).

[10] Glaser, *Z. Elektroch.*, **9**, 11 (1903).

H_2O but easily decomposed with the precipitation of basic salts. The same is true of platinic nitrate. Platinic chloride, bromide and sulfate are soluble in water. The chloroplatinites of Na (Na_2PtCl_4) and Ba are soluble; of Zn, K and NH_4^+, sparingly soluble; of Pb and Ag, insoluble in H_2O. K_2PtCl_4 is more soluble in H_2O than is K_2PtCl_6 (see below). Cyanoplatinites of the alkali and alkaline earth metals and all of the cyanoplatinates are soluble in H_2O. Many of the chloroplatinates are soluble in H_2O, including those of Na (Na_2PtCl_6), Ba, Sr, Mg, Zn, Al and Cu; those of K and NH_4^+ are slightly soluble in H_2O, insoluble in ethanol.

6. **Reactions.** — *a.* Sodium hydroxide forms with $PtCl_2$ a precipitate of $Pt(OH)_2$ (cf. 4) soluble in excess of the reagent to Na_2PtO_2 ($Na_2Pt(OH)_4$), which is readily reduced by ethanol to platinum black (cf. 1). Platinic chloride, a brown-red solid, forms with KOH or NH_4OH,[1,2] not too dilute, a yellow, crystalline precipitate of K_2PtCl_6 and $(NH_4)_2PtCl_6$ respectively, insoluble in ethanol, slightly soluble in H_2O, soluble in an excess of the alkalis and reprecipitated by HCl. Potassium carbonate and $(NH_4)_2CO_3$ give the same precipitate, insoluble in excess of the reagent. A more complete precipitation of the K^+ or NH_4^+ is obtained by use of their chlorides. The corresponding sodium salt, Na_2PtCl_6, is very soluble in H_2O and decomposed by light in alkaline solution, forming PtO_2.

b. Oxalic acid does not reduce platinum salts (distinction from Au). KCN forms with Pt^{+4} a yellow, crystalline precipitate of $Pt(CN)_4$, readily soluble in excess of the reagent. Pt^{++} and Pt^{+4} both form series of complex salts, e.g., $Pt(CN)_4^{--}$, $Pt(CN)_6^{--}$, $Pt(CN)_4(OH)_2^{--}$, and $Pt(CN)_n(X)_{6-n}^{--}$ (where X may be a halogen), etc. $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ do not affect Pt^{++}; with $PtCl_4$ both give precipitates of K_2PtCl_6. The ferrocyanide in excess gives first a green precipitate, then, with still more reagent, a yellow solution.[3] Thiocyanates form with Pt^{++} thiocyanoplatinites, e.g., $K_2Pt(CNS)_4$; with Pt^{+4}, thiocyanoplatinates, e.g., $K_2Pt(CNS)_6$.

c. Pt^{++} and Pt^{+4} form a series of complex nitrites. (Cf. 5, *c*.)

d. Hypophosphites reduce $PtCl_4$ to $PtCl_2$ without formation of Pt°.[4] Phosphates do not form precipitates with platinum salts.

e. Hydrosulfic acid precipitates, from Pt^{++} solutions, brownish to black PtS, insoluble in acids, slightly soluble in H_2O and alkali sulfides. Ammonium sulfide in excess forms $(NH_4)_2PtS_3$. With H_2S, Pt^{+4} salts form PtS_2, black,[5] slowly soluble in alkali sulfides, insoluble in acids except aqua regia, readily converted, on exposure to air, to $PtOS \cdot xH_2O$. Sulfur dioxide decolorizes a solution of $PtCl_4$, giving a product which does not respond to the usual reagents for Pt and requires long boiling with HCl for the removal of the SO_2.[6] Soluble sulfates do not form precipitates with Pt^{++} or Pt^{+4}, but basic salts may be formed.[7] Sodium thiosulfate, in warm acid solution, causes the precipitation of PtS.

f. In general, halides form complex salts with both ions of platinum, the formulas being M_2PtX_4 and M_2PtX_6, where M is a univalent metal or its equivalent and X is Cl, Br, or I. The chlorides of K^+ and NH_4^+ form yellow chloroplatinates, K_2PtCl_6 and $(NH_4)_2PtCl_6$, slightly soluble in H_2O, insoluble in ethanol. A method for the quantitative estimation of the two alkalis is based on this reaction. The bromide or iodide is less satisfactory (see below). KI colors a solution of $PtCl_4$ red to brown (sensitive to less than 0.0_51 g. Pt), and may precipitate black platinic iodide, PtI_4. Excess of the reagent forms K_2PtI_6, brown, slightly soluble, and unstable.[8]

g. Arsine passed into $PtCl_4$ gives a black precipitate, possibly the arsenide, $PtAs_2$.

[1] For the compounds of NH_3 with Pt salts, see Werner, "New Ideas on Inorganic Chemistry," translated by Hedley. Longmans, Green and Co., New York, **1911**.

[2] If excess NH_4OH is added to a solution of $H_2PtCl_2(OH)_4$, fulminating platinum, $NH_3Pt_2(OH)_{10}$ is formed. Jacobsen, *Compt. rend.*, **149**, 574 (1909).

[3] Meldrum, *Ch. News*, **78**, 270 (1898). Cf. Vitali, *Boll. ch. farm.*, **45**, 665 (1906).

[4] Sieverts, *Z. anorg. allgem. Ch.*, **64**, 56 (1909); Cf. Sieverts, *Z. Ch. Ind. Kolloide*, **12**, 263–8 (1913).

[5] Cf. Antony and Lucchesi, *Gazz. ch. ital.*, **26**, 211 (1896).

[6] Birnbaum, *Ann.*, **159**, 116 (1871).

[7] Blondel, *Ann. ch. phys.*, [8] **6**, 81 (1905).

[8] Cf. Peterson, *Z. anorg. allgem. Ch.*, **19**, 59 (1898).

Arsenites and arsenates give precipitates with Pt^{+4}, soluble in HNO_3.[1] Stannous chloride colors a solution of Pt^{++} deep red and reduces Pt^{+4} to Pt^{++}. Small amounts of $SnCl_2$ with dilute Pt solutions give a golden yellow color.[2]

h. Ferrous sulfate boiled with Pt^{+4} precipitates Pt°, the reduction being hindered by acids, but helped by $HgCl_2$ or NO_3^-.

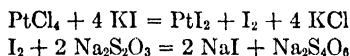
7. Ignition. — All platinum compounds, upon ignition, are reduced to the metal. Owing to its high melting point (cf. 1) and to the difficulty with which it is attacked by most chemicals, platinum has an extended use in the chemical laboratory for evaporating dishes, crucibles, wire, etc.[3]

8. Detection.[4] — *a.* Platinum is identified by the appearance of the reduced metal, by its insolubility in HCl or HNO_3 and solubility in aqua regia, by its formation of a precipitate with NH_4Cl and KCl, by its reaction with $SnCl_2$ (6, *g*) (distinction from Ir, Pd, Au, or Fe); or by its reaction with KI (6, *c*). (Fe, Cu, and oxidizing agents interfere.) Au and Pt may be separated from other cations by precipitation with hydrazine sulfate or chloride in an HCl solution. The precipitate will contain only Au, Pt, Hg and some Cu.[5] Pt is separated from Au by boiling with oxalic acid and $(NH_4)_2C_2O_4$, which precipitates the Au, leaving the Pt in solution. The filtrate should be evaporated, ignited, and the residue examined for solubility in HCl or HNO_3; if soluble only in aqua regia, the solution may be tested with NH_4Cl. If the Au and Pt have been precipitated in the second group with H_2S and dissolved in $(NH_4)_2S_2$, they may be separated from As, Sb and Sn by dissolving the reprecipitated sulfides in HCl + $KClO_3$, evaporating to remove the Cl_2, and, after addition of excess KOH, boiling with chloral hydrate, which precipitates the Au and Pt, leaving As, Sb and Sn in solution. The precipitate may also be dissolved in aqua regia and treated as above. $FeSO_4$ may be used to separate Au and Pt from As, Sb and Sn.

b. Organic reagents. — Benzidine acetate produces a flocculent, blue precipitate with Pt salts in dilute solution.[6] An aqueous solution of dimethylamine gives a yellow precipitate with concentrated solutions of Pt^{+4}. Solutions of Pt^{++} or Pt^{+4} in quinoline decompose on heating.[7] $PtCl_4$ yields a precipitate with gelatin but not with agar agar.[8] Diacetyldioxime precipitates Pt incompletely and then only on boiling.

9. Determination.[9] — *a. Gravimetrically*, platinum may be precipitated as Pt°, PtS_2,[10] $(NH_4)_2PtCl_6$, or K_2PtCl_6 and, after ignition, weighed as the metal.

b. Volumetrically, platinum may be determined by treating $PtCl_4$ with excess KI and titrating the liberated iodine with thiosulfate.[11]

$$PtCl_4 + 4\,KI = PtI_2 + I_2 + 4\,KCl$$
$$I_2 + 2\,Na_2S_2O_3 = 2\,NaI + Na_2S_4O_6$$

c. Platinum is seldom determined electrolytically.

[1] Reichard, *Ber.*, **27**, 1027 (1894).

[2] Ruer, *Z. Elektroch.*, **14**, 310 (1908); Wöhler with Spengel, *Z. Ch. Ind. Kolloide*, **7**, 243 (1910); Hulett, *Phys. Rev.*, **33**, 310 (1911); Langstein and Prausnitz, *Ch. Ztg.*, **38**, 802 (1914).

[3] Due, however, to the high price since 1914, many substitutes have come into use; e.g., quartz, certain alloys, tantalum, etc.

[4] See: Mylius and Mazzucchelli, *Z. anorg. allgem. Ch.*, **89**, 1 (1914); Davis, *Bur. Mines Tech. Paper* 270, **1921**.

[5] Christensen, *Z. anal. Ch.*, **54**, 158 (1915).

[6] Malatesta and Di Nola, *Boll. ch. farm.*, **52**, 461–3 (1913).

[7] Beckmann, *Z. anorg. allgem. Ch.*, **51**, 236 (1906).

[8] Bancroft, *J. Phys. Ch.*, **14**, 220 (1910).

[9] For analysis of Pt alloys see: Arnold, *Z. anal. Ch.*, **51**, 550 (1912); of platinum earths see: Duparc, *Ibid.*, **60**, 48 (1921); *Helv. Ch. Acta*, **2**, 324 (1919); Burgess and Sale, *Ind. Eng. Ch.*, **6**, 452 (1914); Anon., *Ch. Eng. Mining Review*, **20**, 142–3, 170–1 (1928).

[10] Gaze, *Apoth. Ztg.*, **27**, 959 (1912); Ivanov, *J. Russ. Phys. Ch. Soc.*, **48**, 527 (1916).

[11] Peterson, *Z. anorg. allgem. Ch.*, **19**, 59 (1899).

10. Oxidation and Reduction.[1] — Solutions of platinum salts are reduced to the metallic state by Pb, Ag, Hg, Sn (Sn^{++} to Pt^{++} only), Bi, Cu (Cu_2^{++} to Pt^{++}), Cd, Zn, Fe, Fe^{++}, Co and Ni. Many organic compounds reduce platinum ions to Pt°, e.g., formic acid, glycerin in NaOH solution, and hydrazine in alkaline or acetic acid solution. On the other hand, SO_2, oxalic acid and hydroxylamine do not reduce Pt^{+4} to Pt°. The same is true of alkaline peroxides.

§75. Molybdenum (Greek, *molybdos* = lead). Mo = 96.0. Atomic No. 42. Valence 2, 3, 4, 5 and 6. Discovered by Scheele in 1778.

1. Physical Properties. — Density, 10.21 ± 0.03;[2] melting point, 2622° ± 10°.[3] Pure Mo° is a silvery white, tough, malleable metal, softer than glass.[4] It is not oxidized by air or water at ordinary temperatures, but upon heating in air it becomes brown, then blue, and finally, above 600°, burns to the white oxide, MoO_3. The principal use of Mo° is in alloy steels, where 0.2%–0.75% is said to impart deep hardness, toughness, etc.[5] Smaller amounts are used in electric lamps, radio tubes, and, as MoO_3, in the preparation of fine colors, inks, and a reagent for phosphorus.

2. Occurrence. — Molybdenum is not found native, but occurs chiefly as molybdenite, MoS_2; wulfenite, $PbMoO_4$; as the oxide, MoO_3, in molybdenum ochre; and as pateraite, $CoMoO_4$, more recently developed. While workable deposits are widely scattered over the earth's surface, in recent years practically the entire production has been confined to Colorado, where MoS_2, equivalent to about 1520 long tons of Mo°, was mined in 1928. The price that year was about $2.25 per pound.

3. Preparation.[6] — (1) Molybdenum may be obtained from MoS_2 by roasting to MoO_3, leaching with ammonia water to give $(NH_4)_2MoO_4$, igniting to MoO_2[7] and conversion to Mo° by the thermite process.[8] (2) Fusion of the ore, in a lead blast furnace, with Na_2CO_3 and carbon, yields a slag of Na_2MoO_4 which may be used in the electric furnace to produce ferromolybdenum, perhaps the most important commercial form of the metal.[9]

4. Oxides and Hydroxides. — While many oxides and hydroxides have been described in the literature, there is some question as to the existence of several of them. Molybdic oxide, MoO_3,[10] is found in nature (cf. 2). It is generally white when obtained by heating Mo° (cf. 1) or treating molybdates with HNO_3; yellow when hot; a greenish yellow after ignition. It sublimes readily to give small, colorless crystals. Predominantly an "acidic" oxide, it dissolves readily in alkalis to form molybdates which combine with excess MoO_3 to produce very complex molecules. For example, NH_4OH with MoO_3 is said to give $(NH_4)_2MoO_4$; the commercial ammonium molybdate is, however, $(NH_4)_6Mo_7O_{24}$, which may be written $3(NH_4)_2MoO_4 \cdot 4MoO_3$.[11] Two hydrates of

[1] Marie, *Compt. rend.*, **146**, 475 (1907).

[2] Davey, *Phys. Rev.*, [2] **25**, 753 (1925).

[3] Worthing, *Ibid.*, p. 846.

[4] Impurities have a marked influence on these properties.

[5] Gillett and Mack, "Molybdenum, Cerium and Related Alloy Steels," Chemical Catalog Co., Inc., New York, **1925**; Hopkins, "Chemistry of the Rarer Elements," D. C. Heath and Co., New York, **1923**, pp. 248–55; Pokorny, "Molybdän," Wilhelm Knapp, Halle (Saale), **1927**, p. 130, *et seq.*

[6] Pokorny, *loc. cit.*, p. 62 *et seq.*; Abegg, IV, 1, 2, **1921**, pp. 494–8. Both are especially good on the general subject of molybdenum.

[7] Biltz and Gärtner, *Ber.*, **39**, 3370 (1906).

[8] *Ibid.*

[9] Cf. Braun, *Metallbörse*, **19**, 2190–1 (1929); *C.A.* **23**, 5425.

[10] Hantzsch, *Z. Elektroch.*, **24**, 201 (1918).

[11] See, however: Klason, *Ber.*, **34**, 153 (1901); Forsen, *Compt. rend.*, **172**, 215 (1921); Posternak, *Ibid.*, **171**, 1058, 1213 (1920); **172**, 114 (1921); Abegg, IV, 1, 2, p. 577.

MoO_3 have been described, white $MoO_3 \cdot H_2O$ (or H_2MoO_4), and yellow $MoO_3 \cdot 2H_2O$ (or $H_2MoO_4 \cdot H_2O$).[1] Molybdenum dioxide, MoO_2, brown (sometimes blue), is obtained by reduction of $(NH_4)_2MoO_4$ (cf. 2) or MoO_3;[2,3] the sesquioxide, Mo_2O_3, black, results when the higher oxides are treated with Zn or Na-amalgam. The hydroxides, $Mo(OH)_4$[4] and $Mo(OH)_3$, have been described as dark red and brownish black, respectively. The entire subject needs further investigation, however.

5. Solubilities.[5] — *a. Metal.* — Molybdenum is soluble in hot dilute HCl; soluble in concentrated H_2SO_4 at 200–250°; readily soluble in HNO_3[6] with oxidation to MoO_3; soluble in cold aqua regia, more rapidly on heating; not affected by fused non-oxidizing alkalis.

b. Oxides and Hydroxides. — Mo_2O_3 is insoluble in acids; $Mo(OH)_3$ dissolves with difficulty. MoO_2 is insoluble in HCl, attacked by HNO_3 or fused NaOH. MoO_3 is more soluble in cold than in hot H_2O; soluble in alkalis, forming the corresponding molybdate; if unfused, more or less soluble in all acids; if fused, insoluble in HCl, soluble in concentrated H_2SO_4 and in HF. Fusion decreases its solubility in NH_4OH.

c. Salts. — The salts of the lower valences of Mo are nearly all soluble in water, oxidizing, however, on exposure, to Mo^{+6}. Alkali molybdates are soluble in H_2O, the others insoluble. Solutions of the alkali molybdates are decomposed by acids, forming MoO_3, which dissolves in excess of the acid.

6. Reactions.[7] — *a.* The molybdenum salts of lower valence give precipitates with alkali hydroxides and carbonates, forming the corresponding hydroxide or basic oxide. These compounds oxidize in the air to the so-called blue molybdenum molybdate.[8] Normal molybdates, as R_2MoO_4, readily form acid salts or complex polymolybdates; for example, heating MoO_3 with Na_2CO_3 gives trimolybdates, $R_2O \cdot 3MoO_3$, and tetramolybdates, $R_2O \cdot 4MoO_3$.

b. Mo^{+3} gives no precipitate with oxalic acid,[9] a dark gray precipitate with acetates, a complex ion with CN^- and CNS^-, e.g., $Na_3Mo(CNS)_6 \cdot nH_2O$. $K_4Fe(CN)_6$ gives a dark brown, $K_3Fe(CN)_6$ a red-brown, precipitate. Mo^{+4} forms complex cyanides.[10] Oxalic and acetic acids form complex ions with Mo^{+6} from which HCl in excess does not precipitate molybdic oxide. $K_4Fe(CN)_6$ forms a red-brown precipitate in MoO_4^{--} solutions acidified with HCl; CNS^- produces a yellow color, changing to a deep carmine red upon addition of a reducing agent, e.g., Zn, $SnCl_2$, etc. The color is not affected by H_3PO_4 (distinction from Fe^{+3}, which will not interfere if the duration of the reducing action is sufficient to leave only Fe^{++}). Tartaric and other organic acids interfere.[11]

c. Nitric acid oxidizes all lower valences of Mo to Mo^{+6}, and precipitates, from solu-

[1] Hüttig, *Z. angew. Ch.*, **35**, 391 (1922) gives a résumé of the acids of Mo. Cf. Hüttig and Kurre, *Z. anorg. allgem. Ch.*, **126**, 167 (1923); Burger, *Ibid.*, **121**, 240 (1922).

[2] Guichard, *Compt. rend.*, **129**, 722 (1899).

[3] Heated with NH_4Cl, MoO_3 gives MoO_2.

[4] The correct formula may be $MoO(OH)_2$. Cf. Paal, *et. al.*, *Ber.*, **47**, 2214 (1914); **48**, 220 (1915).

[5] Ruder, *J. Am. Ch. Soc.*, **34**, 387 (1912).

[6] Concentrated HNO_3 induces passivity, probably due to a protective coating of MoO_3.

[7] For reactions of molybdates see: Amadori, *Atti. accad. Lincei*, [5] **22**, i, 609 (1913); Arnal, *Ann. ch. anal. ch. appl.*, **34**, 97–103 (1929); *C.A.* **23**, 3186.

[8] Friend, VII, 3, p. 131; Wardlaw and Nicholls, *J. Ch. Soc.*, **127**, 1311, 1487 (1925); Abegg, IV, 1, 2, pp. 621–9.

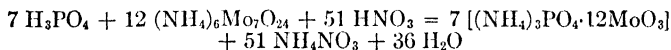
[9] Spittle and Wardlaw, *J. Ch. Soc.*, **1928**, 2742–56, *C.A.* **23**, 2898, consider the complex oxalates of Mo.

[10] Abegg, IV, 1, 2, pp. 528–34 gives $R_4[Mo(OH)_4(CN)_4]$ aq., and $[R_4Mo(CN)_8]$ aq. Cf. Friend, VII, 3, p. 170 *et seq.*

[11] For reaction using Zn see: Moir, *J. Ch. Met. Soc. S. Africa*, **16**, 191 (1916), *C.A.* **10**, 1825; using $SnCl_2$, which gives a sensitivity of 1 : 625,000, see: Stěrba-Böhm, *et al.*, *Z. anorg. allgem. Ch.*, **110**, 81 (1920). For complex thiocyanates of Mo see: James and Wardlaw, *J. Ch. Soc.*, **1928**, 2726–39.

tions of molybdates, molybdic oxide,[1] soluble in excess of the reagent. The composition of the precipitate apparently depends upon conditions (cf. 4). H_2O_2 added to an acid molybdate solution produces a yellow color not extracted by ether (vanadates and titanates interfere); in ammoniacal solution the color is red brown, due to the formation of a permolybdate.[2]

d. Phosphoric acid and its salts precipitate, from strong HNO_3 solutions of ammonium molybdate,[3] somewhat slowly, more rapidly on warming, ammonium phosphomolybdate,[4] yellow, of variable composition,[5] soluble in NH_4OH and other alkalis, slightly soluble in excess PO_4^{-3}:

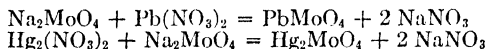
$$7\,H_3PO_4 + 12\,(NH_4)_6Mo_7O_{24} + 51\,HNO_3 = 7\,[(NH_4)_3PO_4 \cdot 12MoO_3] + 51\,NH_4NO_3 + 36\,H_2O$$

Arsenates give the same reaction, ammonium arsenomolybdate being formed.[6] The sensitivity of the test is affected by Cl^-, tartaric acid and reducing agents.

e. Neutral and alkaline solutions of MoO_4^{--} are colored yellow or brown by S^{--}, due to the formation of thiomolybdates.[7] MoS_3 is precipitated upon acidification. Acid solutions of MoO_4^{--}, treated with a small amount of S^{--}, give a blue color but no precipitate; treated with more H_2S, a brown precipitate of MoS_3 slowly forms, the reaction being complete only under pressure or at 100°. The precipitate is soluble in $(NH_4)_2S_x$, especially when warm and not too concentrated, forming ammonium thiomolybdate,[8] from which acids reprecipitate the trisulfide, soluble in HNO_3, insoluble in boiling oxalic acid (distinction from W, separation from SnS_2), and in concentrated HCl. If $Na_2S_2O_3$ be added to a solution of $(NH_4)_2MoO_4$, slightly acidified, a blue precipitate and blue colored solution are obtained. If the acidity is greater, a red-brown precipitate forms.[9] An acid solution of MoO_4^{--}, treated with H_3PO_2 and H_2SO_3, gives an intense bluish-green precipitate or color, depending upon the amount of Mo present.

f. Halogen compounds are not important in the analysis of molybdenum.

g. Sodium arsenate forms with Mo^{++} a gray precipitate of molybdous arsenate; with Mo^{+3}, molybdic arsenate; with MoO_4^{--}, a series of heteropoly-acids, as does phosphorus[10] (cf. *d*). Ammonium arsenomolybdate in appearance is not readily distinguished from the corresponding phosphomolybdate. Precipitation of the arsenic compound does not take place until the solution is slightly warmed, while in the case of the phosphate, separation begins even in the cold. It is not certain that Sb may be substituted for As or P in these reactions. Stannous salts give with $(NH_4)_2MoO_4$ a blue solution (§71, 6, *k*).

h. The alkali molybdates are soluble in H_2O and precipitate from solution nearly all other metallic ions, forming molybdates.

$$Na_2MoO_4 + Pb(NO_3)_2 = PbMoO_4 + 2\,NaNO_3$$
$$Hg_2(NO_3)_2 + Na_2MoO_4 = Hg_2MoO_4 + 2\,NaNO_3$$

[1] The same reaction takes place with hydrochloric, but not with sulfuric, acetic, oxalic or tartaric acid.

[2] Cf. Komarowsky, *Ch. Ztg.*, **37**, 957 (1913).

[3] Concerning the formula for ammonium molybdate, see Abegg, IV, 1, 2, pp. 607–10. For preparation of a stable solution of $(NH_4)_2MoO_4$ see: Mehlig, *Chemist-Analyst*, **17**, No. 4, 6 (1928).

[4] Svanberg and Struve, *J. prakt. Ch.*, **44**, 299 (1848), Struve, **54**, 288 (1851), discovered this important reaction. For formula see: Rosenheim and Jänicke, *Z. anorg. allgem. Ch.*, **100**, 304 (1917).

[5] Posternak, *Compt. rend.*, **170**, 930 (1920).

[6] Maderna, *Atti. accad. Lincei*, [5] **19**, ii, 15 (1910), discusses the precipitation of arseno-molybdates.

[7] Abegg, IV, 1, 2, p. 651 *et seq.*

[8] Abegg, *loc. cit.*

[9] Falciola, *Ann. ch. appl.*, **17**, 261–2 (1927).

[10] Rosenheim, *et al.*, *Z. anorg. allgem. Ch.*, **84**, 217 (1913).

7. Ignition.[1] — With microcosmic salt,[2] in the outer blowpipe flame, all compounds of Mo give a bead which is yellow to green while hot and colorless on cooling; in the inner flame a brown bead appears, opaque if much Mo is present. On charcoal, in the outer flame, MoO_3 is vaporized as a white incrustation; in the inner flame — better with Na_2CO_3 — metallic Mo is obtained as a gray powder, separable from the mass by washing. Dry molybdates form a blue mass when heated on a Pt foil with concentrated H_2SO_4 to vaporization of the latter and then cooled in air. Vapor from the breath often assists in development of the color.

8. Detection.[3] — *a.* In the ordinary process of analysis, Mo appears in the arsenic division of Group II, along with As, Sb, Sn, Au and Pt. Like As_2S_5, MoS_3 is insoluble in concentrated HCl, soluble in HNO_3; hence after precipitation from $(NH_4)_2S_x$ and solution in HNO_3, the As may be removed with magnesia mixture and Mo detected in the filtrate by means of the phosphomolybdate test (cf. 6, *d*),[4] the CNS^- test (cf. 6, *b*), etc.

b. Organic reagents. — Tannin gives a deep red to brown color with MoO_4^{--} in alkaline solution.[5] An acid solution of MoO_4^{--}, treated with excess phenylhydrazine in acetic acid (1:4 of 50% $HC_2H_3O_2$), gives a deep red color or a red precipitate when boiled.[6] (Tungstate, vanadate and chromate do not interfere.) An alcoholic solution of diphenylcarbazide gives a deep blue-violet color when added to a dilute solution of MoO_4^{--}; excess reagent produces a precipitate; excess acid or base interferes, but W, V and Ti do not. An alkali molybdate in acetic acid solution gives an orange color with pyrogallol or pyrocatechol, and a deep blue with quinol (or hydrazine). A very sensitive reagent for MoO_4^{--} is potassium ethyl xanthate[7] in acetic acid, which will give a deep red color when added dropwise to a solution containing as little as 0.0_64 g. of Mo per cc. Malowan[8] recommends the use of a freshly prepared reagent, but Koppel states[9] that the appearance of the color is merely hastened thereby. The intensity of the color is proportional to the amount of Mo present, and is unaffected by Ti, V, or W; CrO_4^{--} should be reduced to Cr^{+3}. Oxalate, Cu, Co, Ni, Fe and UO_2^{++} also interfere.

9. Determination.[10] — *Gravimetrically*, Mo may be precipitated and weighed, as $PbMoO_4$.[11] In a sufficiently acid solution, this forms a separation from the common elements, but V and W interfere. Precipitation as MoS_3 and ignition to MoO_3 has been recommended by Binder[12] and others. While precipitation as mercurous molybdate and ignition to MoO_3 is recommended, the method is of more limited application. *Volumetrically*, Mo may be determined by titration with $KMnO_4$[13] after reduction to Mo^{+3} in a Jones reductor or by means of SO_2.[14] *Electrolytically*, Mo may be precipitated as hydrated Mo_2O_3 from H_2SO_4 or HCl solution, ignited to MoO_3 and weighed.[15]

[1] Rüdisüle, II, p. 247 *et seq.*

[2] Borax is unsatisfactory because the tests are not very delicate.

[3] Cf. Noyes and Bray, *J. Am. Ch. Soc.*, **29**, 137-205 (1907).

[4] Unsatisfactory with small amounts of Mo.

[5] Moir, *loc. cit.*

[6] Spiegel and Maass, *Ber.*, **36**, 512 (1903); Pozzi-Escot, *Ann. ch. anal. ch. appl.*, **12**, 92 (1907).

[7] Tamchyna, *Ch. Listy*, **24**, 465–6 (1930), *C.A.* **25**, 2661, suggests the cetyl alcohol derivative to increase the sensitivity of the test.

[8] Malowan, *Z. anorg. allgem. Ch.*, **108**, 73 (1919).
Cf. *Z. anal. Ch.*, **79**, 201–4 (1930); *C.A.* **24**, 1054.

[9] Koppel, *Ch. Ztg.*, **43**, 777 (1919).

[10] See especially: Bonardi and Barrett, "Determination of Molybdenum," Bur. Mines Tech. Paper 230, **1920**.

[11] This method, suggested by Chatard, *Am. J. Sci.*, [3] **1**, 416 (1871), was commended by Brearley and Ibbotson as one of the most stable processes found in analytical chemistry.

[12] Binder, *Ch. Ztg.*, **42**, 255 (1918); cf. Moser and Behr, *Z. anorg. allgem. Ch.*, **134**, 49 (1924); Brinton and Stoppel, *J. Am. Ch. Soc.*, **46**, 2454 (1924).

[13] Cf. Kassler, *Z. anal. Ch.*, **75**, 457–66 (1928); *C.A.* **23**, 1078.

[14] For use of $TiCl_3$ see: Willard and Fenwick, *J. Am. Ch. Soc.*, **45**, 928 (1923).

[15] Wherry and Smith, *J. Am. Ch. Soc.*, **29**, 806 (1907).

10. Oxidation and Reduction. — All lower valence forms of Mo are readily oxidized to Mo^{+6} by HNO_3 or ignition. Some forms are oxidized merely upon exposure to the air. Many reducing agents, both organic and inorganic,[1] react with Mo^{+6} to give ions of lower valence, the particular one depending upon the reagent and conditions; usually, however, a mixture is obtained, e.g., "molybdenum blue."

THE COPPER GROUP (SECOND GROUP, DIVISION B)

MERCURY (IC), LEAD, BISMUTH, COPPER, CADMIUM, (RUTHENIUM, RHODIUM, PALLADIUM, OSMIUM)

§76. Bismuth (Ger., *Wiesemutung* = Wismut). Bi = 209.00. Atomic No. 83. Valence 3 and 5. Discovered by Valentine in 1450.

1. Physical Properties. — Density, 9.80 ± 0.03 (X-ray method);[2] melting point, 271.0° ± 0.15°;[3] boiling point, 1506° (calc.),[4] 1490° (measured).[5] Bi commences to volatilize below 1200°, for at that temperature the vapor pressure is 102 mm.[6] It is very brittle; somewhat malleable; not very ductile; and when bent at 100° it crackles like tin. It is silver colored with a reddish tinge, lustrous, diatomic in the solid state, monatomic in the vapor,[7] hardness 2–2.5 (Moh's scale), thermal conductivity low (Ag : Bi : : 100 : 1.8), electrical conductivity good.[8] Bi serves for the preparation of many pharmaceutical products and cosmetics, and is also employed for the manufacture of low melting alloys, e.g., one, consisting of Bi, Pb, Sn and Cd (15, 8, 4 and 3 parts respectively), melts at 60°.

2. Occurrence. — While bismuth is a fairly common element, it is not abundant or widely distributed. It is usually found native, often associated with Sn, Co or Au ores. Bolivia is the chief producer. It is said that this source alone could furnish one ton a day. (The world's consumption is about 270 tons a year.) Bismuth and its sulfide, bismuthinite, Bi_2S_3, are the principal ores, and bismuth ochre or bismite, Bi_2O_3, is the commonest oxidation product.

3. Preparation. — Bismuth is one of the troublesome impurities in Pb, Cu and Sn ores, special refining processes being necessary when it is present. In case of Pb ores, Bi is not removed by either the Parkes or Harris process. An electrolytic method is there-

[1] E.g., Zn°, H°, alkali amalgams, Sn°, Sn^{++}, Cu°, Cu_2^{++}, Fe^{++}, SO_2, N_2H_4, I^-, Ti^{+3}, $S_2O_3^{--}$, cane sugar, etc. Cf. Canneri, *Gazz. ch. ital.*, **60**, 113–25 (1930), *C.A.* **24**, 3723.

[2] Davey, *Phys. Rev.*, [2] **25**, 753 (1925).

[3] Mylius, *et al.*, *Z. anorg. allgem. Ch.*, **96**, 261 (1916); Schulze, *Z. tech. Physik*, **10**, 16–23 (1930); *C.A.* **24**, 2027.

[4] Van Liempt, *Z. anorg. allgem. Ch.*, **114**, 105 (1920).

[5] Ruff and Bergdahl, *Ibid.*, **106**, 94 (1919).

[6] Greenwood, *Proc. Roy. Soc.*, **A83**, 486 (1910); *C.A.* **5**, 2756.

[7] Johnsen, *Centr. Min. Geol.*, **1916**, 385; *C.A.* **12**, 1777.

[8] For a general survey see: Schulze, *Z. Metallkunde*, **16**, 48 (1924); *C.A.* **18**, 3309.

fore necessary, leaving Bi in the sludge (anode). From these slimes the two companies operating electrolytic Pb refineries produce all of the metallic Bi made in the United States.[1]

4. Oxides and Hydroxides. — Bi_2O_3, (BiO, Bi_2O_4, BiO_2, Bi_2O_5).[2] Bismuth trioxide, Bi_2O_3, pale yellow to brownish, is formed by heating metallic Bi to its boiling point in contact with air, or by ignition of $Bi(OH)_3$. The most convenient method is to heat the basic nitrate (in air) to constant weight. Other oxides of Bi have been reported, as (a) the suboxide or monoxide, BiO;[3] (b) the tetroxide, Bi_2O_4, yellow to brown, obtained by oxidation of the trioxide in alkaline solution;[4] (c) the pentoxide, $Bi_2O_5 \cdot H_2O$ (or $HBiO_3$), scarlet red, obtained by oxidation of Bi_2O_3 in very concentrated alkali, most conveniently done electrolytically.[5] When heated the pentoxide decomposes, giving off O_2 at as low as 150° and leaving Bi_2O_3. Alkali bismuthates have been reported. They are either unstable compounds or mixtures.[6]

5. Solubilities. — *a. Metal.* — HNO_3 is the proper solvent for Bi. At 65° the reaction is essentially: $2\ Bi + 8\ HNO_3 = 2\ Bi(NO_3)_3 + 4\ H_2O + 2\ NO$.[7] (Apparently some HNO_2 should be present to initiate the reaction.) Metallic bismuth is insoluble in HCl in the absence of O_2 ($4\ Bi + 3\ O_2 + 12\ HCl = 4\ BiCl_3 + 6\ H_2O$); is not affected by H_2S[8] or by cold or dilute H_2SO_4;[9] is soluble in hot, concentrated H_2SO_4, $2\ Bi + 6\ H_2SO_4 = Bi_2(SO_4)_3 + 3\ SO_2 + 6\ H_2O$. The solubility of Bi in acids, especially HCl and $HC_2H_3O_2$, is markedly increased by addition of H_2O_2 (30%). Aqua regia readily dissolves Bi, giving $BiCl_3$. With Cl_2 there is slight action unless a trace of moisture is present, then $BiCl_3$ is formed with or without production of light, depending upon the fineness of the Bi powder, temperature, etc. Heated in Br_2 vapor, $BiBr_3$ is formed. Iodine reacts directly with hot Bi, forming BiI_3. Bi may be alloyed readily with Cd, Hg, Fe, Sn, Pb, Cu, Ag and the Pt metals.

b. Oxides and Hydroxides. — Bismuth oxide, Bi_2O_3, and the hydroxides, $Bi(OH)_3$ and $BiO(OH)$, are soluble in HCl, HNO_3 and H_2SO_4; insoluble in water[10] and the alkali hydroxides[11] or carbonates, as well as in NH_4OH. The solubility product of freshly precipitated bismuth hydroxide is 4.3×10^{-31}.[12] The hydroxide is soluble in alkali solutions in the presence of glycerol, tartrates, or citrates. The solubility of $BiOOH$ in H_2O at 20° is about 0.00144 g./l.[13] $Bi_2O_4 \cdot H_2O$ may be converted into alkali salts and heavy metal salts, from which HNO_3 reprecipitates the oxide. It is not affected by NH_4OH; only slowly attacked by cold, dilute mineral acids; energetically decomposed by concentrated acids. The oxide reacts very slowly with H_2SO_3 giving $Bi_2(SO_4)_3$. It is not decomposed by cold dilute H_2SO_4; is attacked slowly by cold dilute HNO_3, readily by cold concentrated acids; is decomposed at −15° by concentrated HCl, with evolution of Cl_2 and formation of $BiCl_3$; is not affected by NH_4OH; is insoluble in concentrated KOH. Bi_2O_5, upon long contact with H_2O, forms hydrates of the lower oxides. The dry pentoxide exhibits weak acid properties; is somewhat soluble in concentrated alkalis

[1] For details of extraction and purification see: Mellor, IX, p. 593–99.

[2] Hutchins and Lenher, *J. Am. Ch. Soc.*, **29**, 31 (1907).

[3] Bismuth monoxide (BiO), dark gray, is obtained by treating the hydroxide, suspended in 2% KOH, with stannite. Schneider, *J. prakt. Ch.*, [2] **60**, 524 (1899).

Neusser, *Z. anorg. allgem. Ch.*, **138**, 180 (1924), states that BiO is $Bi_2O_3 + Bi°$. The dark precipitate is washed free from tin by decantation and dried in a vacuum over H_2SO_4.

[4] Gutbier and Bünz, *Sitzber. Phys. Med. Soc. Erlangen*, **39**, 172; **40**, 96 (1908).

[5] Deichler, *Z. anorg. allgem. Ch.*, **20**, 81 (1899).

[6] Ruff, *Z. anorg. allgem. Ch.*, **57**, 220 (1908); *C.A.* **2**, 1936.

[7] Stansbie, *J. Soc. Ch. Ind.*, **25**, 47 (1906); **27**, 365 (1908); **32**, 314 (1913).

[8] Tammann and Köster, *Z. anorg. allgem. Ch.*, **123**, 220 (1922).

[9] Gutbier, *J. prakt. Ch.*, [2] **78**, 425 (1908).

[10] Almkvist, *Z. anorg. allgem. Ch.*, **103**, 240–2 (1918).

[11] Moser, *Ibid.*, **61**, 384 (1909), gives the solubility in NaOH at 20° as 0.04 g./l.

[12] Bayerle, *Rec. trav. ch.*, **44**, 518 (1925).

[13] Almkvist, *loc. cit.*

with formation of the corresponding bismuthate,[1] (Bi_2O_5 is reprecipitated upon acidification); is insoluble in dilute HNO_3 and H_2SO_4; is decomposed with formation of $Bi(NO_3)_3$ when heated in 65% HNO_3. In concentrated H_2SO_4 and fuming HNO_3, it is soluble at 0°; slightly soluble in dilute HF, readily soluble in the concentrated acid;[2] soluble in HCl with evolution of Cl_2 and formation of $BiCl_3$; soluble in excess HI with evolution of I_2 and formation of $HBiI_4$; attacked by H_2S to form Bi_2S_3, by H_2SO_3 to give $Bi_2(SO_4)_3$.

c. Salts. — Many of the bismuth salts are insoluble in water. Most of those that are soluble hydrolyze to form an insoluble[3] oxy-salt. In such cases, presence of the corresponding free acid will prevent the hydrolysis,[4] e.g., $BiCl_3$, $BiBr_3$, $Bi(NO_3)_3$, $Bi_2(SO_4)_3$ will dissolve readily in a dilute solution of HCl, HBr, HNO_3 or H_2SO_4, respectively.[5] Bismuth chloride, bromide and sulfate are deliquescent; the nitrate less so.[6]

6. Reactions. — *Water.* — A solution of $BiCl_3$ in water, acidified with HCl, yields, upon dilution, a precipitate of bismuthyl chloride, BiOCl: $BiCl_3 + H_2O \rightleftarrows BiOCl + 2\ HCl$. The precipitate is white, insoluble in tartaric acid (distinction from Sb), completely converted by H_2S into Bi_2S_3. Bismuthyl bromide, BiOBr, white, and bismuthyl iodide, BiOI, red, are prepared like the chloride. The bromide is decomposed into a mixture of the normal and basic sulfate on prolonged interaction with concentrated H_2SO_4.[7] The bromide is insoluble in aqueous KI and reduces an acid solution of $KMnO_4$. The iodide is decomposed by concentrated H_2SO_4 or HNO_3, giving I_2; is not affected by $HC_2H_3O_2$, alkalis, or H_2S. The presence of acetic, citric, and other organic acids prevents the precipitation of Bi^{+3} when an excess of water is added. When bismuth nitrate is allowed to crystallize from hot HNO_3, the pentahydrate, $Bi(NO_3)_3{\cdot}5H_2O$, is produced. When treated with cold H_2O, the gelatinous precipitate first formed becomes crystalline. If air dried, the dihydroxynitrate, $Bi(OH)_2NO_3$ is obtained. Hot water converts this into bismuthyl hydroxynitrate, $(BiO)_2(OH)NO_3$. The same compound is obtained when bismuth nitrate is treated with hot or cold water until no more HNO_3 is extracted.[8] A solution of $Bi(NO_3)_3$, on diluting with water, forms a pre-

[1] The products formed have not been definitely determined. In fact, the whole bismuthate question is open. Perhaps there are only two oxides, Bi_2O_3 and Bi_2O_5, others reported being mixtures. Perhaps the bismuthates are merely oxides with adsorbed or absorbed alkali.

[2] Fischer and Thiele, *Z. anorg. allgem. Ch.*, **67**, 316 (1910).

[3] Regarding the solubility of BiOCl, see: Noyes, *et al.*, *J. Am. Ch. Soc.*, **39**, 2526 (1917).

[4] Probably complexes are formed, as $HBiCl_4$ or H_2BiCl_5, the product depending on the amount of acid present.

[5] The above should not be interpreted to imply that only the specific acid is effective. Hydrogen ions will prevent hydrolysis, however introduced, although the halides require more free acid to form stable solutions than does the nitrate.

[6] Regarding the solubility of Bi_2S_3 in alkaline sulfides, see: Knox, *J. Ch. Soc.*, **95**, 1760 (1909).

[7] Thomas, Ann. ch. phys., [7] **13**, 163 (1898); Gmelin, 8th ed., No. 19, p. 155.

[8] Quartaroli, *Gazz. ch. ital.*, **43**, I, 97 (1913). The nitrate is a complicated system, by no means as simple as the statements in the text above might lead one to believe.

cipitate of BiOCl when a few drops of HCl are added. Bismuth sulfate, $Bi_2(SO_4)_3$, is hydrolyzed slowly by cold water, rapidly by hot water, forming dibismuthyl sulfate, $(BiO)_2SO_4$ (perhaps some $Bi(OH)SO_4$).

a. The alkali hydroxides precipitate from solutions of bismuth salts, bismuth hydroxide, $Bi(OH)_3$,[1] white, becoming yellow on boiling, due to the formation of BiO(OH); insoluble in water; only slightly soluble in excess alkalis[2] (distinction from Sb and Sn); insoluble in NH_4OH (distinction from Cu and Cd); slightly soluble in NH_4Cl; reduced to the metal by alkaline formaldehyde, $2\ Bi(OH)_3 + 3\ CH_2O + 3\ NaOH = 2\ Bi + 3\ HCOONa + 6\ H_2O$. Bismuth hydroxide is not precipitated from solutions containing glycerol, tartaric, or citric acid. All precipitates of $Bi(OH)_3$ contain some of the corresponding oxy-salt. Alkali carbonates precipitate white bismuthyl carbonate, $(BiO)_2CO_3$,[3] containing more or less hydroxide and other impurities. Alkaline earth carbonates react in a similar way The precipitate is insoluble in excess of the reagent.

b. Oxalic acid and soluble oxalates precipitate white bismuth oxalate, $Bi_2(C_2O_4)_3$,[4] soluble in strong acids if not too dilute. Bismuth acetate is of minor importance.[5] Soluble cyanides form bismuth cyanide, which is rapidly hydrolyzed to $Bi(OH)_3$, insoluble in excess reagent, soluble in acids as above. Ferrocyanides give a yellowish white precipitate; ferricyanides, a yellow to brown precipitate, both soluble in HCl; concentrated CNS^- gives a reddish-brown solution (best obtained with the solid reagent)

c. Bismuth nitrate has been discussed above.

d. Hypophosphorous acid gives a white precipitate of bismuth hypophosphite, $Bi(H_2PO_2)_3$, which slowly turns gray — hastened by heating — giving metallic Bi,[6] $3\ Bi(H_2PO_2)_3 = 2\ Bi + Bi(PO_3)_3 + 6\ P + 9\ H_2O$. Phosphorous acid precipitates white bismuth phosphite, $Bi_2(HPO_3)_3{\cdot}3H_2O$, practically insoluble in water, not affected by fixed alkalis, slowly decomposed by KI, and acted upon at once by H_2S.[7] Ortho-phosphates quantitatively precipitate Bi^{+3} from a nitrate solution as bismuth phosphate,[8] $BiPO_4$, white; insoluble in dilute HNO_3 (sp. g. 1.02); readily soluble in concentrated HCl; partially decomposed by boiling with NH_4OH; completely decomposed by alkali hydroxides.[9] From solutions of the

[1] Hackspill and Kieffer, *Ann. ch.*, [10] **14**, 227–82 (1930), *C.A.* **25**, 258–61, state that $Bi^{+3} + NH_4OH$ gives $(Bi_2O_3)_2{\cdot}N_2O_5{\cdot}H_2O$, and conclude that $Bi(OH)_3$ does not exist.

[2] Moser, *Z. anorg. allgem. Ch.*, **61**, 384 (1909).

[3] Vanino, *Pharm. Zentralhalle*, **52**, 761 (1911).

[4] Moles and Portillo, *Anales soc. españ. fís quím.*, **21**, 401 (1923); **22**, 187 (1924), *C.A.* **18**, 362, 2294.

[5] For the preparation, analysis, etc., of bismuth acetate see: Späth, *Monatsh.*, **33**, 243 (1912).

[6] Vanino and Hartl, *J. prakt. Ch.*, [2] **74**, 150 (1906).

[7] Vanino and Hartl, *loc. cit.*

[8] Stähler, *Ch. Ztg.*, **31**, 615 (1907).

[9] Kürthy and Müller, *Bioch. Z.*, **147**, 378 (1924), *C.A.* **19**, 529.

chloride, H_3PO_4 gives no precipitate. Soluble phosphates, however, do form a precipitate (soluble in HCl). Bismuth pyrophosphate, $Bi_4(P_2O_7)_3$, white, is obtained when $Bi(NO_3)_3$ is treated with $Na_4P_2O_7$. It is soluble in excess reagent, decomposed, on warming, to $BiPO_4$; insoluble in $HC_2H_3O_2$; soluble in hot HCl or HNO_3; decomposed by hot H_2SO_4. Metaphosphoric acid and metaphosphates give a white precipitate of bismuth metaphosphate, $Bi(PO_3)_3$, if, after mixing, the solution is made alkaline with NH_4OH. The precipitate is readily converted to $BiPO_4$ by boiling.

e. Hydrosulfic acid and soluble sulfides precipitate from dilute acid solutions[1] dark brown bismuth sulfide, Bi_2S_3, insoluble in cold, dilute mineral acids and alkali sulfides, but soluble in hot dilute (2 *N*) HNO_3 and hot concentrated HCl. The precipitate from alkaline solution, or that produced by alkaline sulfides is soluble in an excess of the alkali sulfide, the solubility varying with the $[OH^-]$.[2] The solubility in water is 0.35×10^{-6} mols./l. at 18°.[3] Bi_2S_3 is insoluble in alkali cyanides. It reacts with ferric salts, $Bi_2S_3 + 6\ FeCl_3 = 2\ BiCl_3 + 3\ S + 6\ FeCl_2$. Ammonium thioacetate, added to a cold, acidic solution of Bi^{+3}, incompletely precipitates the bismuth as Bi_2S_3. Precipitation is complete on boiling. Sodium thiosulfate, when heated with a solution containing Bi^{+3}, precipitates Bi_2S_3. Sodium hyposulfite, $Na_2S_2O_4$, in excess, precipitates from slightly acid solutions, Bi_2S_3 contaminated with sulfur and Bi°. A large excess of reagent or acid results in the precipitation of Bi° at room temperature.[4] Sulfurous or sulfuric acid does not give a precipitate with Bi^{+3}. Any precipitate formed upon addition of salts of these two acids is probably due to hydrolysis rather than the separation of an insoluble sulfate of Bi.

f. BiF_3 is the most stable of the halogen compounds, not hydrolyzed by water, soluble in hot HCl, HNO_3, or H_2SO_4; soluble in excess HF[5] and fluorides;[6] readily soluble in anhydrous acetone,[7] but insoluble in water or alcohol. Hydrochloric acid and soluble chlorides give a precipitate of bismuth oxychloride, BiOCl,[8] white, in solutions of $Bi(NO_3)_3$ not containing too much free acid. (This explains the occasional precipitation of Bi in Group I.) The precipitate is readily dissolved by addition of more acid (distinction from the Group I chlorides), forming $HBiCl_4$ or H_2BiCl_5, depending upon the amount of acid used.[9] Bismuth oxychloride is de-

[1] Ramachandran, *Ch. News*, **131**, 135, 294, 386 (1925).
[2] Knox, *J. Ch. Soc.*, **95**, 1760 (1909).
[3] Weigel, *Z. physik. Ch.*, **58**, 293 (1907).
[4] Brunck, *Ann.*, **336**, 288 (1904).
[5] Fischer and Thiele, *Z. anorg. allgem. Ch.*, **67**, 316 (1910).
[6] Von Helmolt, *Ibid.*, **3**, 145 (1893).
[7] Vournazos, *Ibid.*, **150**, 153, 155 (1926).
[8] Herz and Bulla, *Ibid.*, **61**, 389 (1909); **63**, 60 (1909); Dubrisay, *Compt. rend.*, **148**, 831; **149**, 451–3 (1909).
[9] Noyes, *et al.*, *J. Am. Ch. Soc.*, **39**, 2526 (1917).

composed by the fixed alkalis, $BiOCl + NaOH = BiOOH + NaCl$.[1] Hydrobromic acid and soluble bromides do not precipitate bismuth from solutions of $BiCl_3$, but from $Bi(NO_3)_3$ they precipitate white bismuth oxybromide, BiOBr, which, by long treatment with water, is converted to Bi_2O_3.[2] The oxybromide is soluble in HCl, HBr and HNO_3; difficultly soluble in concentrated H_2SO_4; converted by the fixed alkalis to BiOOH (see above). The presence of KBr prevents the precipitation of BiOCl by H_2O,[3] and also dissolves any oxychloride already precipitated. Hydriodic acid and soluble iodides precipitate from solutions of Bi^{+3} (unless strongly acid) dark brown bismuth iodide, BiI_3, which is readily soluble in excess of reagent, forming yellow BiI_4^-.[4] The BiI_3 is reprecipitated and slowly hydrolyzed by addition of H_2O.[5] Prolonged boiling gives red bismuth oxyiodide, BiOI, which is soluble in HCl, decomposed by HNO_3 or H_2SO_4, converted to the oxide by fixed alkalis, not affected by $HC_2H_3O_2$ or KCl. BiI_3 is decomposed by HNO_3, giving I_2; is not affected by H_2S in absence of water; is quickly converted to Bi_2S_3 by alkali sulfides. Dry BiI_3 is decomposed by fixed alkalis, giving Bi_2O_3 and iodide.[6] The complex thallous penta-iodobismuthite, Tl_2BiI_5, red, soluble in 20,000 parts of H_2O, is formed by adding KI to an acidic solution containing Tl^+ and Bi^{+3}.[7] (This reaction is recommended for detection of Bi.) Sodium chlorate added to a warm solution of $Bi(NO_3)_3$ gives, on cooling, a white precipitate of bismuth oxychlorate, $BiOClO_3$.[8] Sodium bromate and iodate both give white precipitates with solutions of $Bi(NO_3)_3$; the bromate is readily soluble, the iodate slightly soluble in HNO_3. The composition of neither bromate nor iodate has been definitely determined.[9]

g. Bismuth arsenite, $BiAsO_3$, is obtained by treating a bismuth nitrate-mannite solution with H_3AsO_3 or an alkali arsenite. The precipitate is readily soluble in HNO_3, not affected by NaOH or Na_2CO_3.[10] Bismuth arsenate is obtained by treating a bismuth nitrate-mannite solution with H_3AsO_4 or an alkali arsenate. The precipitate is readily soluble in HCl, less so in HNO_3; slowly decomposed by hot NaOH.[11] Alkali stannite,

[1] Jellinek and Kühn, *Z. physik. Ch.*, **105**, 346 (1923).

[2] MacIvor, *Ch. News*, **30**, 190 (1874).

[3] A moderately high concentration of KBr is necessary to prevent precipitation on dilution. KCl would do the same thing.

[4] An excellent test for Bi, sensitive to 1 part in a million of H_2O. See Stone, *J. Soc. Ch. Ind.*, **6**, 416 (1887).

[5] Dubrisay, *Compt. rend.*, **149**, 451 (1909).

[6] Gmelin, 8th ed., No. 19, p. 159, says "iodate," but see original ref.

[7] Canneri and Perina, *Gazz. ch. ital.*, **52**, I, 241 (1922).

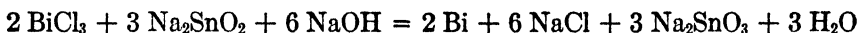
[8] Vanino and Mussgnug, *Ber.*, **50**, 323 (1917).

[9] In case of iodate, it is said that a product of definite composition cannot be isolated.

[10] Vanino and Hartl, *J. prakt. Ch.*, [2] **74**, 143 (1906).

[11] Vanino and Hartl, *loc. cit.*; Valentin, *Z. anal. Ch.*, **54**, 76 (1915).

when added in excess to Bi^{+3}, causes the precipitation of black Bi° (a very delicate test):

$$2\,BiCl_3 + 3\,Na_2SnO_2 + 6\,NaOH = 2\,Bi + 6\,NaCl + 3\,Na_2SnO_3 + 3\,H_2O$$

The stannite is prepared, when wanted, by adding to some $SnCl_2$ enough fixed alkali to redissolve the white precipitate at first formed. (If too much alkali be present, or the system hot, metallic Sn or black stannous oxide may be precipitated.)

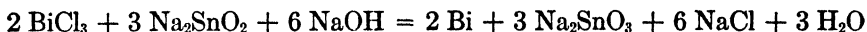
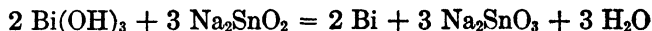
h. Soluble chromates or dichromates added to an acid solution of Bi^{+3} (not too acid) precipitate yellow to orange bismuthyl dichromate, $(BiO)_2Cr_2O_7$;[1] soluble in mineral acids; difficultly soluble in acetic acid; slightly soluble in NaOH unless hot (distinction from $PbCrO_4$). Jackson states that the sensitivity of this chromate test is 1 : 4000.[2]

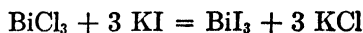
7. **Ignition.** — Heated with charcoal and Na_2CO_3, bismuth is readily separated as the metal from all of its compounds. The globule is easily fusible,[3] brittle (distinction from Pb), and gradually oxidizable in the molten state, forming an incrustation of bismuth oxide (Bi_2O_3), orange yellow while hot, lemon yellow when cold, the edges bluish white when cold. The incrustation disappears in the reducing flame without imparting any color to the outer flame. With borax or microcosmic salt, Bi gives beads, faintly yellowish when hot, colorless when cold.

A mixture of equal parts of Cu_2I_2 and sulfur forms an excellent reagent for the detection of Bi in minerals by use of the blowpipe. The reagent mixed with the unknown is fused on charcoal or a piece of sheet Al. A red sublimate indicates Bi. Mercury gives a mixed red and yellow sublimate. $BiCl_3$ sublimes without decomposition at about 445°, which procedure has been recommended as a separation from Pb.[4]

8. **Detection.**[5] — *a.* Bismuth is precipitated from its solutions, not too acid, by H_2S as Bi_2S_3. Its insolubility in $(NH_4)_2S_x$ gives a separation from the arsenic division of Group II, while its solubility in HNO_3 and non-precipitation with dilute H_2SO_4 separate it from Hg and Pb, respectively. It may then be separated from Cu and Cd, as $Bi(OH)_3$, by precipitation with excess NH_4OH. The precipitate may either be tested directly or dissolved in HCl and the resulting solution tested: (1) Sodium stannite gives a black precipitate of Bi°:

$$2\,Bi(OH)_3 + 3\,Na_2SnO_2 = 2\,Bi + 3\,Na_2SnO_3 + 3\,H_2O$$

$$2\,BiCl_3 + 3\,Na_2SnO_2 + 6\,NaOH = 2\,Bi + 3\,Na_2SnO_3 + 6\,NaCl + 3\,H_2O$$

(2) Potassium iodide in small amount gives a brown precipitate of BiI_3:

$$BiCl_3 + 3\,KI = BiI_3 + 3\,KCl$$

[1] Precipitation is complete in the presence of $NaC_2H_3O_2$.
[2] Jackson, *J. Am. Ch. Soc.*, **25**, 992 (1903).
[3] The melting point of Bi is 271°.
[4] Braly, *Compt. rend.*, **170**, 661 (1920), has discussed blowpipe methods for Bi.
[5] For sensitivity of various tests for Bi, see: Jackson, *loc. cit.*

Any excess reagent dissolves the precipitate, forming the yellow complex ion:

$$BiI_3 + KI = KBiI_4$$

This test is very delicate (see above). (3) Solutions of Bi^{+3} treated with a few drops of HCl and an excess of H_2O, give a white precipitate of BiOCl, insoluble in tartaric acid (distinction from SbOCl). (4) Metallic Zn, Cd, Sn and Fe quickly and completely precipitate metallic Bi, dark gray. (5) Concentrated solutions of CNS^- give a deep reddish-brown color, similar to that of BiI_4^-.

b. A solution of ammonium dithiocarbamate, prepared by shaking CS_2 with concentrated NH_4OH, gives, with Bi^{+3} in neutral or slightly alkaline solution, a yellow-orange precipitate, that becomes rust colored upon adding acetic acid, while the solution becomes yellow.[1] A 5% alcoholic solution of diphenylthiocarbazide gives, with Bi^{+3} in acetic acid, an orange yellow precipitate, insoluble in alkalis. A drop of $BiCl_3$ gives, with solid brucine or a concentrated solution of brucine, a red color of great intensity. Diluted with HCl and then evaporated, the color is more intense; treated with HNO_3 it turns yellow.[2] A solution of $Bi(NO_3)_3$ with Na_2HPO_4 and hematin gives an intense violet color.[3] A slightly acid solution of $Bi(NO_3)_3$ gives with KI and cinchonine[4] an orange precipitate, soluble in alcohol, decomposed by alkalis. The sensitivity is 1 : 500,000; ("free acid" interferes).[5] Hot dilute solutions of $Bi(NO_3)_3$ or $BiCl_3$ give, on addition of diacetyldioxime and NH_3, an intense yellow color or a precipitate. As, Sb, Sn, Co, Mn, Fe all interfere.[6] Cupferron added to Bi^{+3} gives a precipitate practically insoluble in H_2O or mineral acids of moderate concentrations. (Pb and Cd are quantitatively precipitated in neutral solution.)[7] Bi^{+3} is not reduced by hydroxylamine or hydrazine in alkaline solution (distinction from Ag, Hg and Cu).

Many special methods for the detection of Bi have been published. Paneth[8] has advocated the use of radioactive elements. Donau's[9] luminescence method will detect 0.0_61 mg. of Bi.[10]

[1] Parri, *Giorn. farm. ch.*, **73**, 181 (1924).

[2] Reichard, *Ch. Ztg.*, **28**, 1024 (1904); cf. Moser, *Ibid.*, **33**, 309 (1909), who says the reaction is uncertain.

[3] Vasallo, *Gazz. ch. ital.*, **41**, II, 204 (1911).

[4] 1 g. cinchonin is dissolved in 100 cc. H_2O, slightly acidified with HNO_3. After cooling, 2 g. of KI are added.

[5] Feigl, *Z. anal. Ch.*, **62**, 373 (1923); Léger, *Ibid.*, **28**, 347 (1889).

[6] Kubina and Plichta, *Z. anal. Ch.*, **72**, 11 (1927).

[7] Pinkus and Dernies, *Bull. soc. ch. Belg.*, **37**, 267 (1928).

[8] Paneth and Winternitz, *Ber.*, **51**, 1728–43 (1918).

[9] Donau, *Monatsh.*, **34**, 953 (1913).

[10] For additional discussion of a number of characteristic tests for Bi see: Gutzeit, *Helv. Ch. Acta*, **12**, 713–40 (1929); *C.A.* **23**, 4644.

9. Determination. — Bismuth is separated, as $BiPO_4$, from Ag, Cd, Hg, Cu, and Groups III, IV and V; as BiOCl, from all but Ag, Sb, Sn, As; as Bi_2S_3, from Groups III, IV and V. It is weighed as Bi_2O_3, BiOCl, or $BiPO_4$. (a) In the phosphate method,[1] to the hot, acid solution is first added H_3PO_4, then Na_3PO_4, until the system is slightly acid.[2] The solution is filtered through a Gooch filter, the precipitate washed, ignited, and weighed as $BiPO_4$. (b) In the oxychloride method, to the HNO_3 solution is added a little HCl, then the solution is slowly poured into a large volume of water. The precipitate obtained is dried at 105°. Volumetric methods for Bi are of minor importance, the chief one involving precipitation as the basic oxalate and subsequent titration with $KMnO_4$. Colorimetrically, small amounts of Bi may be determined as $KBiI_4$, either with or without the use of cinchonine.[3]

10. Oxidation and Reduction. — Metallic bismuth reduces salts of Hg, Ag, Pt and Au to the metallic state. Bismuth is precipitated as Bi° from solutions of Bi^{+3} by Pb, Sn, Cu, Cd, Fe, Al, Zn, Mg and H_3PO_2 (cf. 6, *d*). Bi^{+3} is oxidized to bismuthate by Cl_2 or H_2O_2 in strong alkaline mixture. All compounds of Bi are reduced to the metal by sodium stannite (cf. 6, *g*). Bismuth chloride or bromide heated in a current of hydrogen, is partially reduced to the free metal. Bi^{+3} is precipitated as Bi° upon warming in alkaline mixture with grape sugar.

§77. **Copper** (Island — *Cyprus*) (Cuprum) **Cu** = 63.57. Atomic No. 29. Valence 1 and 2. Discovery prehistoric.

1. Physical Properties. — Density, 8.93,[4] increased slightly by cold working (rolling or hammering); melting point, 1083.0°.[5] Copper is a yellowish-red metal; it has a greenish tint when molten and in thin sheets transmits a greenish-blue light. Considering the metals in ordinary use, only gold and silver exceed copper in malleability; it has been hammered into sheets 0.0026 mm. thick. Its ductility is also high, the fineness of wire obtainable depends, however, to a large extent on the previous treatment of the metal and the impurities present. Although it ranks next to iron in tenacity, its wire bears about half the weight that an iron wire of the same size will support. The tenacity of Cu increases remarkably by repeated cold extrusion. In heat conductivity it is surpassed only by gold and silver, and, after Ag and Be, is the best conductor of electricity (see §124, 1). The influence of impurities on the electrical conductivity is so marked that quantities almost inappreciable by chemical analysis markedly raise the electrical resistance. Dry air has no action upon copper; in moist air containing CO_2, it becomes coated with a film of "verdigris," which protects it from further action of air or of water. Copper forms a number of very important alloys with other metals: brass (60% or higher Cu — 40% or lower Zn, often small amounts of Pb and Sn); bronze (90% Cu — 10% Sn); German silver (50%–60% Cu — 25% Zn — 15%–25% Ni). About 76% of the Cu mined is used for wire, rods, sheet, and tubes; 24% for brass and other alloys.

2. Occurrence. — Copper is found native in various parts of the world, particularly the Lake Superior district. Native Cu is often 99.9% pure. Copper ores are generally classified as native ores, sulfide ores, and oxidized ores. Some of the minerals are: chalcocite, Cu_2S; bornite, Cu_3FeS_3; chalcopyrite, $CuFeS_2$; tetrahedrite, $M_4^{II}R_4^{III}S_7$; cuprite or red oxide, Cu_2O; malachite, $CuCO_3{\cdot}Cu(OH)_2$; azurite, $2CuCO_3{\cdot}Cu(OH)_2$; chrysocolla, $CuO{\cdot}SiO_2{\cdot}H_2O$. Copper is found chiefly as the sulfide in Montana,

[1] Stähler, *Ch. Ztg.*, **31**, 615 (1907); Luff, *Ibid.*, **47**, 133 (1923).
[2] Rosolic acid may be used as indicator.
[3] For an extensive survey of the field see: Margosches, Vol. X.
[4] Kahlbaum and Sturm, *Z. anorg. allgem. Ch.*, **46**, 217 (1905).
[5] B. Stds. Cir. 35; cf. G. T. S. (1924).

Colorado, Chile, and Spain. The copper content of ores runs as low as 0.3% and as high as 8%. The average for 18 companies is 2.6%. The world's production in 1927 in metric tons of fine blister Cu was: United States, 769,000; Chile, 239,000; Africa, 109,500; Canada, 64,100; Japan, 63,400; Mexico, 57,800; Spain and Portugal, 54,700 (several others, 50,000 each).[1] The price of metallic copper fluctuates considerably. In 1931 it sold lower than six cents per pound, the previous high being around 30 cents per pound. "Lakes" copper usually commands a slight premium.

3. Preparation. — Nearly all Cu ores contain Au and Ag. The recovery of the precious metals as by-products forms, therefore, an important feature of the industry. About 75% of the Cu ore smelted in the United States is first concentrated to a copper content averaging 15%–20%, flotation and gravity methods being widely used. Some ores are leached, not smelted at all.

Three methods may be mentioned: (a) Native Cu ore is crushed, concentrated by washing with water, smelted, and cast into bars. This "Lakes" copper is not further refined, and is used directly for making special brass. (b) Sulfide ores are first crushed, then roasted[2] and smelted to produce a matte containing 40%–50% Cu as Cu_2S, FeS and silica. This molten matte is transferred to a converter, where oxygen and lime are added, the iron silicate slag removed and the sulfur oxidized to SO_2, leaving molten metallic Cu. This is cast into molds. The product is called blister copper and runs 96%–99% Cu. Later it may be remelted and further purified, then cast into anodes (99%–99.3% Cu), about 3 feet square and weighing 500–750 lbs. Subsequent electrolysis, using a bath of $CuSO_4$, gives a cathode running 99.95%–99.98% Cu. These cathodes are melted and cast into shapes for market. Gold and silver are recovered in the anode slimes — they may pay for the entire cost of purification. (c) Copper ores may be crushed then leached with various solvents, such as H_2SO_4, H_2O, NH_4OH, $(NH_4)_2CO_3$, NaCN, etc. The method of recovering Cu from the leach liquor varies with the liquor. Two methods using the H_2SO_4 solution are: (1) addition of Fe gives Cu (H_2SO_4 is recovered and used again); (2) electrodeposition, which is preferable because the Cu is pure. In case of ammonia leaching, the liquor is heated, volatilizing the NH_3 and the Cu is precipitated as CuO which is then reduced and refined.[3]

4. Oxides and Hydroxides. — Cu_2O, CuO, Cu_2O_3, CuO_2. Cuprous oxide, Cu_2O, red, is found native. In the laboratory it may be prepared:[4] (1) by reduction of an alkaline cupric salt, e.g., Fehling's solution heated with an arsenite or glucose gives Cu_2O; (2) by igniting CuO with metallic Cu; (3) reduction of Cu^{++} salts by NH_2OH in alkaline solution.[5] Cuprous hydroxide is said to be precipitated when a fixed alkali is added to a solution of a cuprous salt. According to some authorities, hydrated cuprous oxide, $Cu_2O(H_2O)_n$, is the product. Cupric oxide, CuO, black, is formed: (1) when copper is heated in air; (2) when cupric hydroxide, carbonate, sulfate, nitrate, and certain other salts are ignited in air. Cupric hydroxide is obtained as a precipitate when solutions containing Cu^{++} are treated with a fixed alkali in the absence of tartrate or citrate. It is entirely possible that the compound obtained is not the hydroxide but the hydrated oxide, $CuO{\cdot}H_2O$.[6] Cupric peroxide,[7] CuO_2, and cupric sesquioxide, Cu_2O_3, while believed to have been prepared, have not been isolated.

5. Solubilities. — *a. Metal.* — Dilute nitric acid is the best solvent for copper, although it is more readily dissolved by HNO_2.[8] The major reaction may be represented as follows: $3\,Cu + 8\,HNO_3 = 3\,Cu(NO_3)_2 + 2\,NO + 4\,H_2O$.[9] Copper does

[1] Mineral Ind. **1927.**

[2] Roasting merely lowers the sulfur content.

[3] Burns, *Eng. Mining J.*, **128**, 306–12 (1929), *C.A.* **23**, 5115, gives a detailed description of the electrolytic refining of Cu at Raritan and Great Falls.

[4] Cf. Moser, *Z. anorg. allgem. Ch.*, **105**, 112 (1919).

[5] Moser, *loc. cit.*

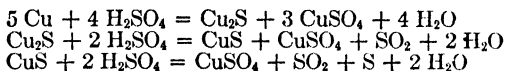
[6] Cf. Weiser, *J. Phys. Ch.*, **27**, 501 (1923).

[7] Aldridge and Applebey, *J. Ch. Soc.*, **121**, 238 (1922).

[8] On the dissolving of Cu in HNO_3 see: Mellor, III, 92; Drapier, *Bull. soc. ch. Belg.*, **27**, 142 (1913), *C.A.* **8**, 32.

[9] See: Bagster, *J. Ch. Soc.*, **119**, 82 (1921), for a different explanation. Using 5 *N* HNO_3, he obtained no NO.

not readily dissolve in acids with evolution of hydrogen; dilute sulfuric acid has only a slight effect; hot and concentrated, it dissolves copper with evolution of SO_2, $Cu + 2 H_2SO_4 = CuSO_4 + SO_2 + H_2O$. This reaction has not been accepted by many workers, due to the fact that the Cu turns black during the process, indicating, according to some, the formation of Cu_2S:[1]

$$5 Cu + 4 H_2SO_4 = Cu_2S + 3 CuSO_4 + 4 H_2O$$
$$Cu_2S + 2 H_2SO_4 = CuS + CuSO_4 + SO_2 + 2 H_2O$$
$$CuS + 2 H_2SO_4 = CuSO_4 + SO_2 + S + 2 H_2O$$

F, Cl,[2] Br and I all attack Cu to an extent increasing apparently, in the order given. HF, HCl, HBr, dry, have very slight effect upon Cu. It is claimed that solutions of these acids appreciably attack Cu only in the presence of air. A hot solution of HCl (15%) dissolves Cu with formation of Cu_2Cl_2 and H_2. Both HBr and HI (aqueous solutions) dissolve copper more readily than HCl. The presence of impurities has a marked effect on the solubility of copper in the above reagents. Cu, but slightly attacked by H_2SO_4, is readily dissolved if a chlorate is added, practically quantitative reduction to the chloride resulting. H_2S has virtually no action, at ordinary temperatures, on finely divided Cu, but if air is present, a vigorous reaction takes place. H_2SO_3 has only a slight effect. Boiling $Na_2S_2O_3$ rapidly converts Cu into Cu_2S. Cold acetic acid slowly dissolves Cu. The glacial acid acts more rapidly, especially in the presence of H_2O_2.[3]

b. Oxides. — Cuprous oxide, Cu_2O, is insoluble in H_2O; soluble in NH_4OH; soluble in excess of fixed alkali. It reacts vigorously with HNO_3. H_2SO_4, H_3PO_4, or cold, very dilute HNO_3, gives $Cu^{\circ} + Cu^{++}$. HF behaves similarly. The oxide dissolves in H_2SO_3 to give Cu_2SO_3; is soluble in HCl and in HI, the latter forming Cu_2I_2. Cupric oxide, CuO, black, and hydroxide, $Cu(OH)_2$, blue, are insoluble in water; soluble in acids; soluble in hot solutions of various ammonium salts; slightly soluble in the fixed alkalis,[4] completely so if tartrate or glycerol be present. The solubility in alkaline tartrate is a separation from Cd and Zn; in NaOH and glycerol, a separation from Cd. Cupric oxide is insoluble in NH_4OH in absence of ammonium salts.

c. Salts. — All salts of copper, except the sulfide, are soluble in NH_4OH. Cuprous salts are generally colorless, though some are yellow, others red. They are soluble in HCl; soluble in cyanides, forming a solution from which sulfides or hydroxides give no precipitate; readily oxidized on exposure to moist air. Cu_2Cl_2 and Cu_2Br_2 are soluble in a solution of NH_4Cl. Cupric salts, in crystals or in solution, are green or blue;[5] anhydrous salts are white. The crystallized chloride and chlorate are deliquescent; the sulfate permanent (efflorescent if the atmosphere is too dry); the acetate efflorescent. Cupric basic carbonate, oxalate, phosphate, borate, arsenite, sulfide, cyanide, ferrocyanide, ferricyanide, and tartrate are insoluble in water. The ammonio salts, the cyanides, and the tartrates are soluble in water. In alcohol, the sulfate and acetate are insoluble — chloride and nitrate, soluble. Ether dissolves the chloride.

[1] For the action of H_2SO_4 on Cu see: Cundall and Fairgrieve, *J. Ch. Soc.*, **105**, 60 (1914); *C.A.* **8**, 1712; Rogers, *Ibid.*, **1926**, 254–69; Druce, *Ch. News*, **136**, 81 (1928); Fowles, *Ibid.*, **136**, 257–9 (1928).

[2] For action of Cl_2 on Cu see: Frommer and Polanyi, *Z. physik. Ch.*, **137**, 201 (1928).

[3] For solubility in NH_4OH see: Yamasaki, *Sci. Reports Tôhoku Imp. Univ.*, **9**, 169–220 (1920), *C.A.* **14**, 3558.

[4] Justin and Müller, *Compt. rend.*, **167**, 779 (1918), give 0.78 g. $Cu(OH)_2$/100 cc. of caustic (density about 1.4). Cf. Müller, *Z. angew. Ch.*, **33**, I, 303 (1920).

[5] Concerning the color of Cu salts see: Denham, *Z. physik. Ch.*, **65**, 641–666 (1909); Garrett, *J. Ch. Soc.*, **103**, 1433 (1913); Poma, *Gazz. ch. ital.*, **40**, I, 176 (1910).

TABLE 35

THE SOLUBILITY OF SOME COPPER SALTS

Salt	Soly. in g./100 g. of soln. at room temp.	Salt	Soly. in g./100 g. of soln. at room temp.
$Cu(ClO_3)_2$	62.17	CuC_2O_4	0.0024–
$CuCl_2$	43.5	CuS	0.0_433
Cu_2Cl_2	1.52	$CuC_4H_4O_6 \cdot 3H_2O$	0.042
$Cu(IO_3)_2$	0.136	$CuCO_3$	0.03
Cu_2I_2	0.0_38	$Cu(OH)_2$	0.0067
$Cu(NO_3)_2$	53.86		

6. **Reactions.** — *a.* Fixed alkali hydroxides precipitate yellow cuprous hydroxide, insoluble in excess reagent. NH_4OH[1] and ammonium carbonate precipitate and redissolve the hydroxide, forming a colorless solution that turns blue on exposure to air; alkalis precipitate cuprous hydroxide from these solutions. Fixed alkali carbonates precipitate yellow cuprous carbonate, Cu_2CO_3.

Fixed alkalis precipitate from solutions of cupric salts, cupric hydroxide, $Cu(OH)_2$,[2] blue, slightly soluble in excess of the base,[3] completely soluble if tartrate, citrate, or certain other organic compounds are present (Fehling's solution). Boiled alone, this solution is fairly stable, but the addition of reducing agents, e.g., glucose, arsenite, etc., causes the precipitation of Cu_2O. Cupric hydroxide is soluble in NH_4OH; soluble in alkali cyanides; changed by boiling to CuO, black. Alkali hydroxides, used in less than equivalent amounts, form insoluble basic salts of a lighter blue than the hydroxide.

Ammonium hydroxide, added in small amount, precipitates pale blue basic salts; in equivalent amount, the deep blue hydroxide (in both cases like the fixed alkalis). The precipitate is soluble in excess of the reagent, forming $(NH_3)_4Cu^{++}$,[4] deep blue (separation from Bi). No precipitate of $Cu(OH)_2$ is obtained if the solution contains a moderate concentration of NH_4^+. The blue color obtained with NH_4OH is a good test for the presence of copper. (Sensitivity, 1 : 25,000; diminished in presence of iron.[5]) Ammonium carbonate gives reactions similar to NH_4OH. Carbonates of the fixed alkalis precipitate greenish blue basic salts, the composition variable, depending upon temperature and concentration;[6] boiling ulti-

[1] Bouzat, *Compt. rend.*, **146**, 75 (1908).

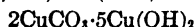
[2] Cf. Hopkins and Beebe, *J. Phys. Ch.*, **34**, 570–9 (1930), who state that the product is $CuSO_4 \cdot 3Cu(OH)_2 \cdot xH_2O$, in case of the sulfate. Conditions of precipitation greatly influence the results, however.

[3] Müller, *et al.*, *Z. physik. Ch.*, **105**, 73–118 (1923), believes Na_2CuO_2 is formed.

[4] Hantzsch and Robertson, *Ber.*, **41**, 4328 (1908); Job, *Compt. rend.*, **184**, 204 (1927).

[5] Ellis and Collier, *J. Ch. Soc.* (*Proc.*), **23**, 264 (1907).

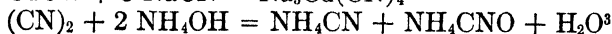
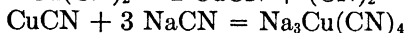
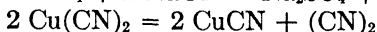
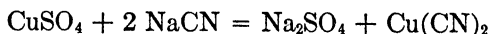
[6] Dunnicliff and Lal, *J. Ch. Soc.*, **113**, 718 (1918). They give the formula:

$$2CuCO_3 \cdot 5Cu(OH)_2$$

Cf. Fonzes and Diacon, *Bull. soc. ch.*, **15**, 723 (1914). Pickering, *J. Ch. Soc.*, **99**, 800 (1911), has done considerable work in the field.

mately gives the oxide, CuO. Carbonates of the alkaline earth metals do not precipitate copper carbonate in the cold; a basic carbonate is precipitated on boiling.

From the blue ammoniacal solutions, the fixed alkalis will precipitate blue cupric hydroxide. Boiling drives off the NH_3 and changes the copper to CuO.

b. Oxalates, cyanides, ferrocyanides, ferricyanides and thiocyanates precipitate their respective cuprous salts from cuprous solutions not too strongly acid. The ferricyanide is brownish, the others are white. The cyanide is readily soluble in excess reagent, from which solution H_2S will not precipitate the sulfide. The thiocyanate is soluble to the extent of 0.0_323 g./l. at 18°,[1] and is used in presence of H_2SO_3 for the quantitative separation of Cu. Soluble oxalates precipitate from solutions of cupric salts, cupric oxalate, bluish white, insoluble in acetic acid (distinction from Cd). The oxalate is formed from mineral acid salts of copper by $H_2C_2O_4$ and alkali acetate. The acetate reduces the $[H^+]$ due to the formation of slightly ionized $HC_2H_3O_2$, thus making the reaction possible. Alkali cyanides precipitate yellowish cupric cyanide, $Cu(CN)_2$, readily soluble in excess, giving $Cu(CN)_4^{--}$ which is unstable, changing to cuprocyanide with liberation of cyanogen. In ammoniacal solution the reaction is said to be: $9\ NaCN + 2\ (NH_3)_4CuSO_4 + H_2O = 2\ Na_3Cu(CN)_4 + NaCNO + (NH_4)_2SO_4 + 6\ NH_3 + Na_2SO_4$. The following steps are given by Kunschert:[2]

$$CuSO_4 + 2\ NaCN = Na_2SO_4 + Cu(CN)_2$$
$$2\ Cu(CN)_2 = 2\ CuCN + (CN)_2$$
$$CuCN + 3\ NaCN = Na_3Cu(CN)_4$$
$$(CN)_2 + 2\ NH_4OH = NH_4CN + NH_4CNO + H_2O$$ [3]

Alkali cyanide also dissolves CuO, $Cu(OH)_2$, the carbonate, sulfide, etc., which change rapidly to cuprocyanide. In these solutions the $[Cu_2^{++}]$ is so low that addition of H_2S forms insufficient Cu_2S to exceed its solubility. Hence this system may be used to separate Cu from Cd, which does give a precipitate. Potassium ferrocyanide precipitates cupric ferrocyanide, $Cu_2Fe(CN)_6$,[4] reddish brown; insoluble in dilute acids; decomposed by fixed alkalis; soluble in NH_4OH.[5] This is a very delicate test for copper.

[1] Prud'homme, *J. ch. phys.*, **9**, 519 (1911).

[2] Kunschert, *Z. anorg. allgem. Ch.*, **41**, 359 (1904).

[3] For additional data see: Moles and Izaguirre, *Anales soc. españ. fís. quím.*, **19**, 33–93 (1921); *C.A.* **15**, 3594; Jennesseaux, *Ann. ch. anal. ch. appl.*, **1**, 15 (1919).

[4] Müller, *et al.*, *J. prakt. Ch.*, **86**, 82 (1912), state that $CuSO_4 + K_4Fe(CN)_6$ gives $K_2Cu_3[Fe(CN)_6]_2 + Cu_2Fe(CN)_6 + K_2CuFe(CN)_6$. The first two are brown, the last yellow.

[5] For the action of NH_4OH on $Cu_2Fe(CN)_6$ see: Crittenden, *J. Am. Ch. Soc.*, **46**, 1210 (1914).

In acid solution, one part of Cu in one million can be detected, in neutral solution, one in 1.5 million, and in neutral solution containing NH_4NO_3 or NH_4Cl, one in 2.5 million.[1] In dilute solution no precipitate separates, the solution becoming pink to red. Potassium ferricyanide precipitates cupric ferricyanide, $Cu_3[Fe(CN)_6]_2$, greenish yellow, insoluble in HCl.

Soluble thiocyanates precipitate black cupric thiocyanate, $Cu(CNS)_2$, unstable, gradually changing to the white cuprous compound (H_2SO_4 hastens the change); soluble in NH_4OH. In the presence of reducing agents, e.g., H_2SO_3, cuprous thiocyanate is precipitated at once (separation from Cd and Zn): $2\ CuSO_4 + H_2SO_3 + 2\ NaCNS + H_2O = 2\ CuCNS + Na_2SO_4 + 2\ H_2SO_4$.

c. Nitric acid rapidly oxidizes cuprous salts to cupric. Cupric nitrite has not been separated from solution; it oxidizes to nitrate on exposure to air; it forms many complex nitrites with other metals.[2]

d. A solution of $CuSO_4$, slightly acidified with HCl, gives a precipitate of cuprous chloride when treated with sodium hypophosphite; if the copper solution is boiled with an excess of the reagent, metallic Cu is precipitated. Cupric hypophosphite, $Cu(H_2PO_2)_2$, white, has been prepared.[3] At 70° $CuSO_4$ reacts with sodium hypophosphite (NaH_2PO_2) to precipitate cuprous hydride which decomposes rapidly. Phosphorous acid precipitates from solutions of cupric acetate, unstable cupric phosphite, $CuHPO_3{\cdot}2H_2O$. Sodium phosphate, Na_2HPO_4, gives a bluish-white precipitate of cupric phosphate, composition apparently variable. Sodium pyrophosphate in excess precipitates $Cu_2P_2O_7{\cdot}2H_2O$, soluble in NH_4OH, mineral acids, and excess reagent; not precipitated in the presence of tartrates or thiosulfates (separation from Cd).

e. Cuprous salts, when boiled with sulfur, give Cu_2S: $2\ Cu_2Cl_2 + S = Cu_2S + 2\ CuCl_2$.[4] Cuprous salts are precipitated or transposed by hydrosulfic acid or soluble sulfides, forming cuprous sulfide, Cu_2S, black, possessing the same solubilities as cupric sulfide.[5] Freshly precipitated Cu_2S transposes $AgNO_3$, forming Ag_2S, Ag° and $Cu(NO_3)_2$; with CuS, Ag_2S and $Cu(NO_3)_2$ are formed. Freshly precipitated sulfides of Fe, Co, Zn, Cd, Pb, Bi, Sn^{++} and Sn^{+4}, when boiled with Cu_2Cl_2 in presence of NaCl give Cu_2S and the chloride of the metal; with $CuCl_2$, CuS and a chloride of the metal are formed, except that SnS gives Cu_2S, Cu_2Cl_2 and Sn^{+4}.

[1] Mellor, III, 103; Szebelledy, *Z. anal. Ch.*, **75**, 167–8 (1928), states that the delicacy of the test is increased and the interference of Fe decreased by the addition of ammonium fluoride.

[2] Kurtenacker, *Z. anorg. allgem. Ch.*, **82**, 204 (1913); Peters, *Ibid.*, **107**, 313 (1919); Cuttica and Gallo, *Gazz. ch. ital.*, **53**, I, 374 (1923).

[3] Engel, *Compt. rend.*, **129**, 518 (1899); cf. Firth and Meyers, *J. Ch. Soc.*, **99**, 1329-33 (1911); Windisch, *Z. anal. Ch.*, **52**, 1 (1913); Neogi and Mukerji, *J. Indian Ch. Soc.*, **6**, 529–45 (1929), *C.A.* **24**, 543.

[4] Pinkard and Wardlaw, *J. Ch. Soc.*, **121**, 1300 (1922).

[5] See: Mellor, III, p. 216, for reactions of Cu_2S.

With cupric salts, H_2S gives CuS,[1,2] black (accompanied by a small amount of Cu_2S + S), produced alike in acid[3] solution (distinction from Fe, Mn, Co, Ni), and in alkaline solution (distinction from As, Sb, Sn). The solubility of CuS is 0.0_333 g./l. at 18°. The precipitate of CuS is easily soluble in 2 N HNO_3, especially if a small amount of nitrite be present (distinction from Hg); dissolved with difficulty by concentrated HCl (distinction from Sb); insoluble in hot dilute H_2SO_4 (distinction from Cd); insoluble in fixed alkali sulfides, and only slightly soluble in yellow ammonium sulfide[4] (distinction from As, Sb, Sn); soluble in solutions of alkali cyanides (distinction from Pb, Bi, Cd, Hg).

When Cu is precipitated as the sulfide it tends to carry down other soluble salts. This is particularly true in the case of Zn. Apparently the acidity and relative concentration of Cu^{++} and Zn^{++} are important factors.[5] Ammonium thioacetate produces a partial precipitation of CuS in cold acid solutions of Cu^{++}, precipitation being complete in hot solutions. $Na_2S_2O_3$,[6] in neutral or acid solution of Cu^{++} gives a reddish-brown precipitate of Cu_2S + S, which gradually becomes black (a distinction from Cd if the solution is fairly acid). Sulfurous acid[7] and soluble sulfites reduce Cu^{++} to Cu_2^{++} This reaction, in slightly acid solution, is important in the thiocyanate method for the determination of Cu.[8]

f. If a small amount of Cu^{++} is added to concentrated HBr, an intense purple color is obtained;[9] claimed to be more sensitive than the ferrocyanide or the sulfide test, detecting 0.0015 mg. of Cu in a drop of the bromide solution. A mixture of sodium bromide and either sulfuric or phosphoric acid may be used in place of the HBr. The reaction probably depends on the formation of $HCuBr_3$ or H_nCuBr_{n+2}. Of the common metals, only iron interferes.

[1] Feigl, *Z. anal. Ch.*, **72**, 32 (1927), states that it is not definitely known whether the precipitate is CuS or Cu_2S + S. In alkaline solution, it is a mixture of CuS + Cu_2S. Gluud, *Ber.*, **55B**, 1760 (1922), says that in 10% ammonia solution, $CuSO_4$ + H_2S + air probably gives S + Cu_2S_2.

[2] For a discussion of the conditions (especially acidity) for precipitation of CuS, see: M. Strell, Dissert., Munich, 1908, p. 24.

[3] CuS precipitates colloidal in a cold solution of low acidity.

[4] Solubility diminished by addition of a small amount of fixed alkali.

[5] Kolthoff and van Dijk, *Pharm. Weekblad*, **59**, 1351 (1922); Scheringa, *Ibid.*, **57**, 1294 (1920).

[6] Roeder, *Tids. Kemi Berg.*, **7**, 94 (1927), *C.A.* **22**, 3596, says that precipitation of Cu with $Na_2S_2O_3$ is complete in presence of HNO_3, HCl, or H_2SO_4. The Cu_2S is washed with cold H_2SO_3. For reaction of cuprous salts with $Na_2S_2O_3$, see: Canneri and Luchini, *Gazz. ch. ital.*, **52**, II, 261 (1922).

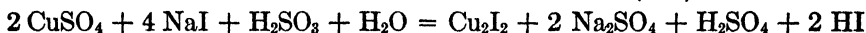
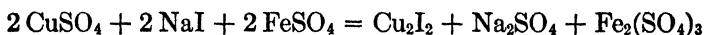
[7] For reactions of Cu^{++} with sulfites see: Baubigny, *Ann. ch.*, **1**, 201 (1914); *Compt. rend.*, **154**, 434 (1912).

[8] Regarding the sulfates of Cu, particularly the basic sulfates, see: Nelson, *J. Phys. Ch.*, **32**, 1185 (1928); Britton, *J. Ch. Soc.*, **1926**, 2868. Britton says that only one compound forms: $4CuO \cdot SO_3 \cdot 4H_2O$.

[9] Sabatier, *Compt. rend.*, **125**, 103 (1897).

Hydriodic acid and soluble iodides precipitate, from concentrated solutions of copper salts, white cuprous iodide, Cu_2I_2, colored yellow to brown by the iodine liberated, $2\,CuSO_4 + 4\,NaI = Cu_2I_2 + I_2 + 2\,Na_2SO_4$. This reaction forms the basis for a quantitative method for the determination of Cu, the liberated iodine being titrated with a standardized reducing agent, e.g., $Na_2S_2O_3$. $I_2 + 2\,Na_2S_2O_3 = Na_2S_4O_6 + 2\,NaI$. Other reactions illustrating the effect of a reducing agent are:

$$2\,CuSO_4 + 2\,NaI + 2\,FeSO_4 = Cu_2I_2 + Na_2SO_4 + Fe_2(SO_4)_3$$

$$2\,CuSO_4 + 4\,NaI + H_2SO_3 + H_2O = Cu_2I_2 + 2\,Na_2SO_4 + H_2SO_4 + 2\,HI$$

Cupric iodate, $Cu(IO_3)_2$, pale blue, is obtained by adding alkali iodate to concentrated $Cu(NO_3)_2$.[1] It dissolves in H_2O to the extent of 0.0033 mols./l. at 25°.

g. Arsenites precipitate from solutions of Cu^{++} salts, other than the acetate, green copper arsenite, composition variable. It is known as Scheele's Green or "Paris Green"; readily soluble in acids and NH_4OH, decomposed by concentrated, fixed alkali. From cupric acetate arsenites precipitate, on boiling, "Schweinfurt" green or "Imperial" green. The composition is generally given as a mixture of cupric arsenite and cupric acetate; readily soluble in NH_4OH and acids; decomposed by fixed alkalis.

Soluble arsenates precipitate cupric arsenate, $Cu_3(AsO_4)_2$, blue green, readily soluble in acids and NH_4OH. Sodium stannite, Na_2SnO_2, added to a cupric salt, gives at first a greenish precipitate of cupric hydroxide, which rapidly changes to cuprous hydroxide, yellowish brown.

h. Dichromates do not give precipitates with cupric salts; normal alkali chromates form a brownish-red precipitate, soluble in NH_4OH or dilute acids.

7. Ignition. — Ignition with Na_2CO_3 on charcoal, leaves Cu° in finely divided grains. The particles are gathered by triturating the charcoal mass in a small mortar, with the repeated addition and decantation of water, until clean Cu° remains. It is recognized by its color and softness when cut. Copper compounds readily dissolve in beads of borax and microcosmic salt, in the outer flame of the blowpipe. The beads are green while hot, and blue when cold.[2] In the inner flame, the borax bead becomes colorless when hot; the microcosmic salt turns dark green when hot, both having a reddish-brown tint when cold (Cu_2O). Compounds of Cu, heated in the inner flame, color the outer flame green. Addition of HCl increases the delicacy of the reaction, giving a greenish-blue color to the flame.

8. Detection. — *a.* Cu is precipitated from its solutions by H_2S, forming CuS. Its insolubility in $(NH_4)_2S_x$ separates it from As, Sb and Sn; its solubility in HNO_3 separates it from Hg. It is separated from lead by

[1] Spencer, *Z. physik. Ch.*, **83**, 290 (1913).

[2] Bancroft and Nugent, *J. Phys. Ch.*, **33**, 729–44 (1929), say that the change in color is due to a change in valence of the copper, blue to green indicating an alteration of Cu^{++} to Cu_2^{++}.

taking advantage of the difference in solubility of the sulfates; from Bi through the formation of a complex $Cu(NH_3)_4^{++}$ ion.

The presence of copper in a solution freed from other ions may be confirmed (1) by the deep blue color of $Cu(NH_3)_4^{++}$ (sensitive to 1 : 25,000), (2) by the formation of brown $Cu_2Fe(CN)_6$, after acidifying with $HC_2H_3O_2$ (see above, 6, *b*), (3) by reduction to metallic copper when a slightly acid solution is boiled with Fe°, (4) by the formation of a purplish-red color when a drop is added to concentrated HBr (cf. 6, *f*),[1] (5) by the reaction with H_2O_2 in presence of $NaHCO_3$[2]. $Ti_2(SO_4)_3$, added to a solution of Cu^{++}, gives a precipitate of Cu° (limit of sensitivity, 1 : 1,000,000).[3]

b. Many tests employing organic reagents have been suggested. Among them are the following: superol (*o*-hydroxyquinoline sulfate),[4] pyramidone,[5] alkali phenolphthalein decolorized by boiling with Zn,[6] benzoinoxime,[7] dinitroresorcinol,[8] guaiac resin (an alcoholic solution),[9] dicyanodiamidine,[10] cupferron[11,12]. A reversal of the Fehling's solution test for arsenic will detect 0.003 g. of Cu in a liter of solution.[13]

9. Determination.[14] — *Gravimetrically*, copper is separated (1) as the metal, electrolytically, from a solution containing 2 cc. H_2SO_4 (95%) and 1 cc. HNO_3 (70%) per 100 cc. of solution, (2) as CuCNS from all elements but Ag, (3) as CuS or Cu_2S, (4) as Cu_2O or Cu° by reduction in fixed alkali solution. Copper is usually weighed as Cu° (after electrolysis),[15] CuO or Cu_2S (after ignition in hydrogen). *Volumetrically*, copper

[1] Cf. Scheringa, *Pharm. Weekblad*, 62, 173 (1925).

[2] To an acid solution of Cu^{++} add $NaHCO_3$ until a slight precipitate persists, then add H_2O_2. The result depends upon the amount of Cu^{++} present; a small amount, e.g., 1 drop of a solution containing 10 mg./cc. in 5 cc. H_2O, gives bright blue, more gives green, and a still larger amount gives a yellowish precipitate, possibly CuOH. Cf. Mayer and Schramm, *Z. anal. Ch.*, **56**, 129 (1917); *J. Ch. Soc.*, **112**, II, 334 (1917).

[3] Knecht, *Ber.*, **41**, 498 (1908).

[4] Saul and Crawford, *Analyst*, **43**, 348 (1918); Schoorl, *Pharm. Weekblad*, **56**, 325 (1919).

[5] Eschauch, *J. pharm. Ch.*, **20**, 49 (1919).

[6] Thomas and Carpentier, *Compt. rend.*, **173**, 1082 (1921). A pink color will appear if there is 1 part of Cu in 100 million present.

[7] Feigl, *Ber.*, **56B**, 2083 (1923). This appears to be a specific reagent for Cu.

[8] Nichols and Cooper, *J. Am. Ch. Soc.*, **47**, 1268 (1925). The reagent will detect 0.004 mg. of Cu in 1 cc. of solution.

[9] Fleming, *Analyst*, **49**, 275 (1924).

[10] Grossmann and Mannheim, *Ch. Ztg.*, **42**, 17 (1918). The product is $(C_2H_5N_4O)_2Cu$. Nickel also gives a precipitate.

[11] Baudisch, *Ch. Ztg.*, **33**, 1298 (1909). This reagent, the ammonium salt of nitrosophenylhydroxylamine, gives a grayish-white precipitate with Cu. Iron interferes.

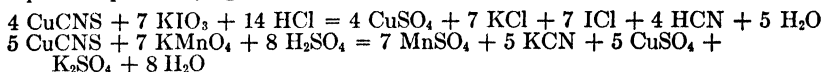
[12] The above list is very incomplete. For further details, see: Rüdisüle, III, 3–30. For a discussion of the sensitivity of the various tests for Cu see: Wöber, *Oesterr. Ch. Ztg.*, **21**, 105 (1919); Pritz, *et al.*, *J. Am. Ch. Soc.*, **35**, 168 (1913); Wagner, *Z. anal. Ch.*, **20**, 349 (1881).

[13] Schenk, *Apoth. Ztg.*, **28**, 137 (1913).

[14] A summary of the application of organic compounds to estimation of Cu and of other metals has been given by Chapman, *J. Ch. Soc.*, **111**, 203 (1917).

[15] Blasdale and Cruess, *J. Am. Ch. Soc.*, **32**, 1264 (1910); Hahn, *Z. anorg. allgem. Ch.*, **99**, 201 (1917). The latter is an exhaustive discussion of the electrolysis in HNO_3.

may be determined (1) by precipitation as Cu_2I_2, the I_2 liberated being titrated with $Na_2S_2O_3$ (cf. 6, *e*);[1] (2) by precipitation as CuCNS, then titration of this compound or its decomposition products, e.g.:

$$4\ CuCNS + 7\ KIO_3 + 14\ HCl = 4\ CuSO_4 + 7\ KCl + 7\ ICl + 4\ HCN + 5\ H_2O$$
$$5\ CuCNS + 7\ KMnO_4 + 8\ H_2SO_4 = 7\ MnSO_4 + 5\ KCN + 5\ CuSO_4 + K_2SO_4 + 8\ H_2O$$

(3) by titration of $Cu(NH_3)_4^{++}$ with alkali cyanide to disappearance of the blue color (cf. 6, *b*). Many modifications of the first two methods have been published.

10. Oxidation and Reduction. — Ions of Cu^{++} and Cu_2^{++} are reduced to Cu° by Zn, Cd, Sn, Al, Pb, Fe, Co, Ni, Bi, Mg, P, and in the presence of NaOH, by SnO_2^{--}. A bright strip of Fe, in a solution of Cu^{++} acidified with HCl, receives a bright copper coating, recognizable when one part of Cu is present in 120,000 parts of H_2O. With a Zn-Pt couple, the Cu is precipitated on the Pt, and its presence can be confirmed by the use of concentrated H_2SO_4 and KBr (see above). Cu^{++} is reduced to Cu_2^{++} by Cu°, by $SnCl_2$ in the presence of HCl, by AsO_3^{-3} and grape sugar in the presence of NaOH, by HI, and by SO_2. Metallic Cu is oxidized to Cu^{++} by solutions of Hg^{++}, Hg_2^{++}, Ag^+, Pt^{+4}, and Au^{+3}, these ions being reduced to the metallic state. Ferric iron is reduced to Fe^{++} by Cu°. Copper is oxidized by many acids.

§78. Cadmium (Gr. *Kadmia* = earth). Cd = 112.41. Atomic No. 48. Valence 2. Discovered by Stromeyer in 1817.

1. Physical Properties. — Density, 8.64 at 16.3°/4°;[2] melting point, 320.9°;[3] boiling point, 766° (calculated).[4] Cadmium is a silvery, crystalline metal, somewhat harder than tin or zinc; more tenacious than tin; malleable and very ductile. It can be easily rolled into foil or drawn into fine wire, but at about 80° it is brittle. Upon bending, cadmium gives the same creaking sound as tin. It is distinctly volatile above 300° and may be readily sublimed, especially in a vacuum, forming silvery white crystals.[5] Cadmium is only slightly tarnished by air and water at ordinary temperatures. When ignited it burns to CdO. When heated, it combines readily with Cl, Br, I, P, S, Se and Te. It forms many useful alloys having low melting points. It is being used for making cadmium solders; as a coating, electrolytically applied, to protect other metals from rusting. Perhaps the most extensive use is to make yellow paint for street cars. The amount of Cd produced in 1928 was nearly 3,000,000 lbs. The metal was quoted at 65 cents per pound in 1931.

2. Occurrence. — Cadmium is found as greenockite, CdS, in Greenland, Scotland, and the United States (Pennsylvania), but the chief source is zinc ores, in which it may be present to the extent of 3%. The ratio of Cd to Zn in the ore is usually about 1 : 400.

3. Preparation. — Almost all of the world's supply of Cd comes from the treatment of impure Zn solutions used for the electrolytic preparation of zinc. Some Cd is produced by the fractional distillation of zinc smelter dust. Since cadmium is somewhat volatile, it is concentrated in the first portion. It is purified electrolytically or by dis-

[1] See: Peters, *J. Am. Ch. Soc.*, **34**, 422 (1912), for sources of error.
[2] Egerton and Lee, *Proc. Roy. Soc.* (*London*), **A103**, 487 (1923).
[3] G. T. S., 1924; Dana and Foote, *Trans. Faraday Soc.*, **15**, 186 (1920).
[4] Millar, *Ind. Eng. Ch.*, **17**, 34 (1925).
[5] Nair and Turner, *J. Ch. Soc.*, **103**, 1534 (1913).

tillation. Cadmium is one of the purest metals obtainable commercially, impurities being easily kept below 0.01%.

4. Oxide and Hydroxide. — Cadmium forms but one[1] oxide, CdO, either by burning of the metal in air or by ignition of the hydroxide, carbonate, nitrate, oxalate, etc. It is a brownish-yellow powder, the exact shade depending somewhat on the mode of preparation. The hydroxide, $Cd(OH)_2$, white, is formed by the action of a fixed alkali upon soluble cadmium salts. It absorbs CO_2 from the air and readily gives up H_2O on heating, forming a mixture of the oxide and hydroxide.[2]

5. Solubilities. — *a. Metal.* — Cadmium dissolves slowly in hot, moderately dilute hydrochloric or sulfuric acid, with evolution of hydrogen; more readily in nitric acid, with evolution of nitrogen oxides. It is soluble in aqueous ammonium nitrate, quietly and without evolution of gas.[3]

b. The oxide and hydroxide are insoluble in water and the fixed alkalis, soluble in ammonium hydroxide; readily soluble in acids, forming Cd^{++}; soluble in a cold mixture of fixed alkali and alkali tartrate, reprecipitated upon boiling (distinction from copper). Freshly precipitated $Cd(OH)_2$ is distinctly soluble in aqueous solutions of the alkali halides and thiocyanates.

c. Salts. — The sulfide, carbonate, oxalate, phosphate, cyanide, ferrocyanide and ferricyanide are insoluble in water, soluble in HCl, HNO_3 and NH_4OH (except CdS which is insoluble in NH_4OH). The chloride and bromide are deliquescent, the iodide is not; all three are soluble in water and alcohol. CdI_2 is one of the few iodides soluble in alcohol. All Cd compounds are soluble in excess of NaI, due to the formation of the complex ion, CdI_4^{--}.

6. Reactions. — *a.* The fixed alkali hydroxides, in the absence of tartaric and citric acids and certain other organic substances, precipitate cadmium hydroxide $Cd(OH)_2$, from solutions of cadmium salts. The product is white, insoluble in excess reagent (distinction from Sn and Zn). Ammonium hydroxide forms the same precipitate, which dissolves in excess. If the concentrated solution of a cadmium salt be dissolved in excess NH_4OH, with gentle heat, and the solution then cooled, crystals of the salt with variable amounts of ammonia are obtained, $Cd(NH_3)_x^{++}$, where $x = 2 - 4$. The fixed alkali carbonates precipitate cadmium carbonate, $CdCO_3$, white, insoluble in excess of the reagent. Ammonium carbonate forms the same precipitate which, however, dissolves in excess. Barium carbonate, in the cold, completely precipitates cadmium as $CdCO_3$ from solutions of its salts.

b. Oxalic acid and oxalates precipitate cadmium oxalate, white, soluble in mineral acids and ammonium hydroxide. Alkali cyanides precipitate cadmium cyanide, $Cd(CN)_2$, white, soluble in excess reagent as $M_2Cd(CN)_4$;[4] ferrocyanides form a white precipitate, ferricyanides, a yellow precipitate, both soluble in HCl and in NH_4OH. Thiocyanates do not precipitate cadmium salts (distinction from copper). Cadmium salts in the presence

[1] Regarding a possible Cd_2O, see: Denham, *J. Ch. Soc.*, **115**, 558 (1919).

[2] Pascal, *Compt. rend.*, **177**, 766 (1923).

[3] Tammann, *Z. anorg. allgem. Ch.*, **121**, 275 (1922).

[4] Masaki, *Bull. Ch. Soc. Japan*, **6**, 60–4 (1931), *C.A.* **25**, 2658, has concluded that the Cd complex is probably $Cd(CN)_3^-$ in all concentrations.

of tartaric acid, are not precipitated by fixed alkalis in the cold; on boiling, CdO is precipitated.

c. HNO_3 dissolves all known compounds of cadmium.

d. Soluble phosphates precipitate cadmium phosphate, white, readily soluble in acids. Sodium pyrophosphate precipitates Cd^{++}; the product is soluble in excess reagent and in mineral acids, not in dilute acetic acid. The reaction is not hindered by the presence of tartrates or of thiosulfates (separation from copper).

e. H_2S and soluble sulfides precipitate, from slightly acid or alkaline solutions, cadmium sulfide, CdS, yellow; insoluble in excess reagent, in NH_4OH or in cyanides (distinction from copper); soluble in 2 *N* HNO_3, hot, dilute H_2SO_4 (1 : 4), and in a saturated solution of NaCl[1, 2] (distinction from copper). Sodium thiosulfate, $Na_2S_2O_3$, does not precipitate Cd^{++} from solution.

f. The non-precipitation by iodide is a distinction from copper. The addition of NH_4ClO_4 to an NH_4OH solution of Cd^{++} gives complete precipitation of the cadmium as perchlorate of the metal ammine, $Cd(NH_3)_4ClO_4$.[3]

g. Soluble arsenites and arsenates precipitate the corresponding cadmium salts, readily soluble in acids and NH_4OH.

h. Alkali chromates precipitate yellow cadmium chromate from concentrated solutions only.

i. A solution of copper and cadmium salts, very dilute, when spread upon a filter paper or porous porcelain plate, gives a ring of the cadmium salt beyond that of the copper salt, easily detected by H_2S.[4]

7. Ignition. — On charcoal, with Na_2CO_3, cadmium salts are reduced before the blowpipe to the metal, and usually vaporized and re-oxidized nearly as fast as reduced, thereby forming a characteristic brown incrustation of CdO. This is volatile by reduction only, being driven with the reducing flame. CdO colors a borax bead yellowish while hot, colorless when cold; microcosmic salt, the same. If fused with a bead of K_2S, a yellow precipitate of CdS is obtained (distinction from Zn).

8. Detection. — *a.* Cadmium is precipitated from its solutions by H_2S, forming yellow (occasionally greenish yellow) CdS. Due to its insolubility in $(NH_4)_2S_x$ and solubility in HNO_3, it is separated with Pb, Bi and Cu from the other metals of Group II. H_2SO_4 removes the Pb^{++}, and NH_4OH the Bi^{+3}, leaving only Cu and Cd in solution. Should Cu be absent, yellow CdS is obtained at once, by treating the ammoniacal solution with H_2S. If Cu is present, an alkali cyanide[5] is added until the

[1] Cushman, *Z. anal. Ch.*, **34**, 371 (1895); Krishnamurti, *J. Ch. Soc.*, **1926**, 1549–55.

[2] For a consideration of the equilibrium between CdS and HCl, see: Aumeras, *J. ch. phys.*, **25**, 727–42 (1928).

[3] Salvadori, *Gazz. ch. ital.*, **40**, II, 19 (1910).

[4] Cf. Feigl, *Microchemie*, **1**, 4–20 (1923).

[5] Daggett, J. Am. Ch. Soc., **51**, 2758–9 (1929) suggests that Cu be precipitated as CuCNS.

solution becomes colorless, whereupon the Cd is detected by the formation of CdS with H_2S (cf. 6, *i*).

b. Organic reagents. — A cadmium salt treated with brucine sulfate (1% solution) and KBr, gives a white precipitate of the double bromide; no precipitate if KCl is used.[1] A few drops of a 5% solution of diphenylthiocarbazide gives a white precipitate when added to a dilute solution of a cadmium salt.[2] A persistent yellow precipitate is produced by boiling an alkaline solution of thiosinamine, to which a salt of cadmium has been added. Uranium is the only metal that interferes.[3, 4]

9. Determination. — (1) Cadmium may be precipitated as the double ammonium phosphate from neutral solution and weighed as $Cd_2P_2O_7$. (2) The hydroxide may be dissolved in KCN and the solution electrolyzed.[5] *Volumetrically*, cadmium is determined indirectly, e.g., by treatment of CdS with I_2 and titration of the excess iodine.

10. Oxidation and Reduction. — Metallic cadmium precipitates the free metal from solutions of Au, Pt, Ag, Hg, Bi, Cu, Pb, Sn and Co; is itself precipitated by Zn, Mg and Al.

[1] Meurice, *Ann. ch. anal. ch. appl.*, [2] **8**, 130–1 (1926).

[2] Parri, *Giorn. farm. ch.*, **73**, 207–14 (1924).

[3] Lemaire, *Répert. pharm.*, [3] **20**, 433–4 (1908), Ann. ch. anal. ch. appl., **14**, 6–7 (1909).

[4] For a more extensive summary of the reactions of cadmium salts with organic compounds, see: Gmelin, 8th ed., No. 33, pp. 141–53; Gutzeit, *Helv. Ch. Acta*, **12**, 713–40 (1929); *C.A.* **23**, 4644.

[5] Flora, *Am. J. Sci.*, [4] **20**, 268, 392, 454 (1905).

§79. Comparison of Certain Reactions of Bismuth, Copper and Cadmium*

	Bi^{+3}	Cu^{++}	Cd^{++}
NaOH	$\underline{Bi(OH)_3}$ white	$\underline{Cu(OH)_2}$ blue	$\underline{Cd(OH)_2}$ white
NH_4OH	$\underline{Bi(OH)_3}$ white	$\underline{Cu(OH)_2}$ blue; $Cu(NH_3)_4^{++}$ (in solution) dark blue	$\underline{Cd(OH)_2}$ white; $Cd(NH_3)_4^{++}$ (in solution) colorless
H_2S (or $(NH_4)_2S$)	$\underline{Bi_2S_3}$ brown black	$\underline{CuS}$ black	$\underline{CdS}$ yellow
KI	$\underline{BiI_3}$ (precipitates, but not from dilute solution) brown black; $KBiI_4$ (in solution) tan	$\underline{Cu_2I_2}$ + I_2 (in solution); white brown	n.v.a.
Fe	$\underline{Bi}$ black	$\underline{Cu}$ red	n.v.a.
Na_2SnO_2	$\underline{Bi}$ black	$\underline{Cu}$ red	$\underline{Cd(OH)_2}$ white (due to NaOH)
Glucose, NaOH, heat	$\underline{Bi}$ black	$\underline{Cu_2O}$ red	$\underline{Cd(OH)_2}$ white (due to NaOH)
H_2O (dilution of concentrated, nearly neutral soln.)	$\underline{BiOCl}$ white	n.v.a.	n.v.a.

* Slightly acid solutions of the chlorides (nitrates or sulfates) may be used.

Notes. — 1. In this table the letters *n.v.a.* mean no visible action; a straight line under a formula indicates that the substance precipitates; a line with up-turned ends, that it is in solution; if both are used, the substance will not precipitate from dilute solution.

2. When two formulas appear in a single square, the upper one indicates the first reaction that occurs; the lower one, the further reaction that takes place with excess of reagent.

3. The text should be consulted for the further chemical and physical properties of these substances.

§79A. Outline of the Analysis of Group II

(Starting with the filtrate from Group I)

Metals, after the removal of Group I, whose sulfides precipitate in 0.25 N HCl (As_2S_5 requires 3–5 N HCl)

Metals	Cu-division: Hg	Pb	Bi	Cu	Cd	As-division: Sn	Sb	As
Ions in acid solution	Hg^{++}	Pb^{++}	Bi^{+3}	Cu^{++}	Cd^{++}	Sn^{++} Sn^{+4}	Sb^{+3} Sb^{+5}	AsO_3^{-3} AsO_4^{-3}
Ions in NaOH solution	—	PbO_2^{--}	—	—	—	SnO_2^{--} SnO_3^{--}	SbO_2^{-} SbO_4^{-3}	AsO_3^{-3} AsO_4^{-3}
Ions in NH_4OH solution	—	—	—	$Cu(NH_3)_4^{++}$	$Cd(NH_3)_4^{++}$	—	—	AsO_3^{-3} AsO_4^{-3}

Reduce $Cr_2O_7^{--}$ and MnO_4^{-} and make 0.25 N with HCl

Hg	Pb	Bi	Cu	Cd	Sn	Sb	As(III)	As(V)
Hg^{++}	Pb^{++}	Bi^{+3}	Cu^{++}	Cd^{++}	Sn^{++} Sn^{+4}	Sb^{+3} Sb^{+5}	AsO_3^{-3}	AsO_4^{-3}
H_2S								
HgS	PbS	Bi_2S_3	CuS	CdS	SnS SnS_2	Sb_2S_3 Sb_2S_5	As_2S_3	AsO_3S^{-3}
$(NH_4)_2S_x$								$HCl+H_2S$
HgS	PbS	Bi_2S_3	CuS	CdS	$(NH_4)_2SnS_3$	$(NH_4)_3SbS_4$	$(NH_4)_3AsS_4$	As_2S_5
HNO_3					HCl			HNO_3
HgS	$Pb(NO_3)_2$	$Bi(NO_3)_3$	$Cu(NO_3)_2$	$Cd(NO_3)_2$	SnS_2	Sb_2S_5	As_2S_5	H_3AsO_4
$HCl+HNO_3$	H_2SO_4				HCl			$NH_4OH+MgCl_2$
$HgCl_2$	$PbSO_4$	$Bi_2(SO_4)_3$	$CuSO_4$	$CdSO_4$	$SnCl_4$	$SbCl_3$	As_2S_5	$MgNH_4AsO_4$
$SnCl_2$	$NH_4C_2H_3O_2$	NH_4OH			divide into 2 parts		HNO_3	
Hg_2Cl_2-Hg	$Pb(C_2H_3O_2)_2$	$Bi(OH)_3$	$Cu(NH_3)_4SO_4$	$Cd(NH_3)_4SO_4$	Fe	Sn–Ag couple	H_3AsO_4	
	$K_2Cr_2O_7$	HCl	divide into 2 parts		$SnCl_2$	Sb	$NH_4OH+MgCl_2$	
	$PbCrO_4$	$BiCl_3$	$HC_2H_3O_2$	NaCN	$HgCl_2$		$MgNH_4AsO_4$	
		KI	$CuSO_4$	$Na_2Cd(CN)_4$	$SnCl_4$ (Hg_2Cl_2)			
		$KBiI_4$	$K_4Fe(CN)_6$	H_2S				
			$Cu_2Fe(CN)_6$	CdS				

DIRECTIONS FOR THE PRECIPITATION AND ANALYSIS OF THE SECOND GROUP (DIVISION A = ARSENIC GROUP, DIVISION B = COPPER GROUP)

§80. In the directions given below it is assumed that Group I has been present and removed in the usual manner, the filtrate being used for the precipitation of Group II. If one wishes to examine a solution directly for Group II, with Group I known to be absent, account must be taken of the reaction of the solution with litmus paper. If the solution is neutral or acid the regular directions may be followed. If it is alkaline it is first made slightly acid with HNO_3 then the regular directions followed. If MnO_4^-, MnO_4^{--}, CrO_4^{--}, or $Cr_2O_7^{--}$ are present they must be reduced by $CH_2O + HCl$ before adjusting the acidity of the solution for precipitation with H_2S.

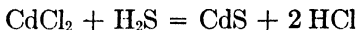
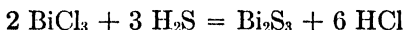
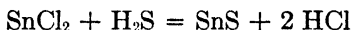
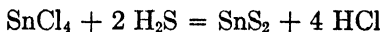
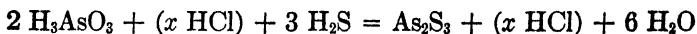
Manipulation. — The filtrate from Group I (§62) (or the original solution, if the metals of the silver group are absent) is examined for MnO_4^- (reddish-purple color) and $Cr_2O_7^{--}$ [orange color, or vanishing blue test on a separate portion of the solution (§131, note 15)]. If either of these is present in moderate or large amounts transfer the solution to a casserole, add 5 cc. of HCl and 2–3 cc. of CH_2O (formaldehyde, 10% solution), and boil.

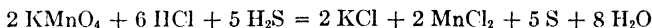
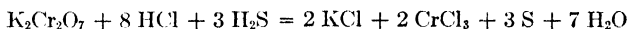
$$2\,KMnO_4 + 6\,HCl + 5\,CH_2O = 2\,KCl + 2\,MnCl_2 + 5\,CH_2O_2 + 3\,H_2O$$

$$K_2Cr_2O_7 + 8\,HCl + 3\,CH_2O = 2\,KCl + 2\,CrCl_3 + 3\,CH_2O_2 + 4\,H_2O$$

After reduction of MnO_4^- and $Cr_2O_7^{--}$ is complete, evaporate it nearly to dryness (not more than 2–3 cc. of liquid left) then dilute with water to 10–15 cc.

Neutralize the solution thus prepared (or the filtrate from Group I if MnO_4^- and $Cr_2O_7^{--}$ are absent), with NH_4OH, adding the reagent a few drops at a time, shaking and then testing with litmus. If the solution becomes alkaline add a few drops of HCl, shake, and test again with litmus. Add 2.5 cc. of 5 *N* HCl, dilute to 50 cc., warm slightly, and pass in H_2S gas for 2–3 minutes (or until the precipitate settles readily). Filter and test the filtrate with more H_2S for completeness of precipitation. After precipitation is complete in this solution, evaporate to a volume of 10–15 cc., add 5 cc. of concentrated HCl (or 10 cc. of 5 *N* HCl), heat to boiling, and treat again with H_2S to precipitate As_2S_5. This precipitate is collected on a separate filter and tested directly for As. Wash the precipitates several times with H_2S water containing a few drops of HCl, then mark the filtrate and set it aside to be tested for the metals of the remaining groups (§127).

$$2\ H_3AsO_3 + (x\ HCl) + 3\ H_2S = As_2S_3 + (x\ HCl) + 6\ H_2O$$
$$SnCl_4 + 2\ H_2S = SnS_2 + 4\ HCl$$
$$SnCl_2 + H_2S = SnS + 2\ HCl$$
$$2\ BiCl_3 + 3\ H_2S = Bi_2S_3 + 6\ HCl$$
$$CdCl_2 + H_2S = CdS + 2\ HCl$$

§81. Notes. — 1. In precipitating Group II with H_2S it is necessary to maintain a certain minimum acidity to prevent the precipitation of some ZnS. If MnO_4^- or $Cr_2O_7^{--}$ were not reduced first, they would be reduced by the H_2S.

$$K_2Cr_2O_7 + 8\ HCl + 3\ H_2S = 2\ KCl + 2\ CrCl_3 + 3\ S + 7\ H_2O$$
$$2\ KMnO_4 + 6\ HCl + 5\ H_2S = 2\ KCl + 2\ MnCl_2 + 5\ S + 8\ H_2O$$

By this reaction the solution might become nearly enough neutral to permit precipitation of sulfides or basic salts of some of the later group metals in Group II.

2. After reduction with HCl and CH_2O it is desirable to evaporate to a small volume, (a) to get rid of excess of CH_2O (which would react with H_2S producing a very unpleasant odor and even a light colored flocculent precipitate of organic sulfides), and (b) to avoid high concentration of Cl^- which interferes with the precipitation of certain of the sulfides of Group II, especially Cd and Pb.

3. If a precipitate forms, on neutralizing with NH_4OH, which fails to redissolve on adding 2.5 cc. of 5 *N* HCl, the precipitate may be disregarded if it is opaque, white, and flocculent or granular. BiOCl and SbOCl frequently appear at this point. They should be left in the solution and treated with H_2S, which will change them to the usual precipitates.

$$2\ BiOCl + 3\ H_2S = Bi_2S_3 + 2\ H_2O + 2\ HCl$$

However, if a gelatinous or colored precipitate is left after the HCl is added, this may be due to later group metals precipitating as hydroxides ($Al(OH)_3$, $Fe(OH)_3$, $Co(OH)_2$, etc.) on neutralization, and not redissolving completely in the amount of acid added. In such a case it is important to warm the solution and add more HCl, a few drops at a time, with shaking, until this foreign precipitate is dissolved.

4. Group II is precipitated from a warm rather than a cold solution (in contrast to Group I) because at the higher temperature the sulfides generally form more granular precipitates which are easier to filter and wash, while the sulfides of As in particular are distinctly slow in coagulating except in a hot solution.

The sulfides are sufficiently insoluble even in the warm solution so that the lower solubility of H_2S in the warm as compared with a cold solution does not interfere seriously with the completeness of precipitation of the group. If the solution is very hot, however, Pb and Cd do not precipitate readily at lower concentrations.

5. Hydrogen sulfide gas should be used in precipitating the metals of the second group. It may be generated in a Kipp apparatus, using ferrous sulfide, FeS, and either dilute commercial sulfuric acid (1–12) or dilute commercial hydrochloric acid (1–1). The gas thus generated should be passed through a wash bottle containing water to remove any acid that may be carried over mechanically. The gas line should always contain a sufficient length of fine bore (0.5 mm.) capillary tubing to limit the maximum rate at which the gas will escape at the outlet to approximately 100 cc. per minute. When only a limited supply of H_2S is needed the system of heating mixtures of S, paraffin and asbestos, may be used.[1] For large supplies the central generator systems of Parsons,[2] and of Barber,[3] may be recommended. The availability of liquid H_2S in recent years (obtainable from The Matheson Co., and The Ohio Chemical Co.) has led to the installation of this

[1] Described by Henwood in *J. Franklin Inst.*, **199**, 685–6 (1925). See, however, Mason, *J. Ch. Ed.*, **4**, 876–8 (1928).

[2] Parsons, *J. Am. Ch. Soc.*, **25**, 231 (1903).

[3] Barber, *J. Ch. Ed.*, **4**, 1546–9 (1927).

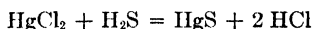
system in many colleges. In this case it is necessary to use a large gasometer (filled from the cylinder of liquid H_2S which is then shut off), from which the gas is piped about the building. This is rather more expensive than the generator system using FeS and HCl or dilute H_2SO_4, but the convenience probably offsets the difference in cost.

6. In treating the unknown solution with H_2S the delivery tube should have a small tip. This breaks the gas up into smaller bubbles causing more effective absorption of the gas by the solution. Precipitation is sometimes carried out under pressure, using for this purpose an Erlenmeyer flask fitted with a two-holed rubber stopper. One hole carries the delivery tube for H_2S, the other is provided with a short piece of glass tubing projecting just past the upper and lower surfaces of the stopper. By placing a finger over this second tube the H_2S can be brought into contact with the solution at greater than atmospheric pressure. To test for completeness of precipitation shut off the H_2S, but keep the tube closed with the finger. On shaking the flask, suction will be felt if the solution absorbs the H_2S from the air space in the flask.

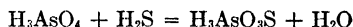
H_2S is poisonous and should be used with care.

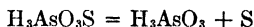
7. The precipitated sulfides of the metals of the arsenic and copper groups (second group) present a variety of colors which aid materially in the further analysis of the group. CdS, SnS_2, As_2S_3 and As_2S_5 are lemon yellow; Sb_2S_3 and Sb_2S_5 are orange; SnS, HgS, PbS, Bi_2S_3, and CuS are black to brownish black. If too much HCl be present, or excessive concentration of Cl^-, lead salts frequently precipitate as the red double salt (§57, 6, *e*). Diluting the solution with 25–30 cc. of H_2O is usually sufficient to convert this to the black PbS. When Hg is present in large amounts it first forms a white precipitate of $HgCl_2 \cdot 2HgS$, changing from yellow to brown and finally black with more H_2S, due to gradual conversion to HgS (§58, 6, *e*). If such an effect is obtained the solution must be treated with H_2S for 1–2 minutes longer before filtering. Otherwise the appreciable solubility of the double salt in HNO_3 may prevent a satisfactory separation of Hg from the other metals of the copper group (§96).

8. In testing for completeness of precipitation with H_2S in the dilute HCl solution, it must be remembered that the more soluble sulfides (Sn, Pb and Cd) do not precipitate promptly if the solution is much more than 0.25 *N* with respect to HCl. Also, the acidity of the solution usually increases as the less soluble sulfides precipitate.

$$HgCl_2 + H_2S = HgS + 2\,HCl$$

Therefore, if a heavy precipitate is obtained the first time, or if no precipitate forms immediately, it may be necessary to dilute the solution with 25–30 cc. of water before treating further with H_2S. A wise precaution at this point is to take a 5 cc. portion of the solution, add 10 cc. of water, and test with H_2S. If no precipitate forms, precipitation is complete except for As.

9. The effect of HCl in promoting the precipitation of As^V by H_2S is quite contrary to its usual behavior. Several explanations have been advanced. The most plausible one is that the concentration of As^{+5} in H_3AsO_4 solution is so low that the sulfide cannot form directly by combination of As^{+5} and S^{--}. The mechanism in this case is, therefore, indirect, involving the formation of mono-thioarsenic acid.

$$H_3AsO_4 + H_2S = H_3AsO_3S + H_2O$$

This compound is fairly stable in dilute acid solution, but decomposes in the presence of moderate or high concentration of HCl. If the current of H_2S is slow the decomposition takes place to some extent according to the equation:

$$H_3AsO_3S = H_3AsO_3 + S$$

This is followed by prompt precipitation of As_2S_3. If the current of H_2S is rapid (ordinary conditions of operation) the decomposition gives As_2S_5:

$$2\,H_3AsO_3S + 3\,H_2S = As_2S_5 + 6\,H_2O$$

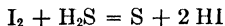
With the acidity 3 *N* or more, precipitation takes place completely and fairly promptly as As_2S_5.

10. The presence of nitrates in the solution may cause considerable trouble when precipitating As^V. In the hot, strongly acid solution part of the H_2S will be oxidized to S, and As_2S_5, temporarily precipitated, may redissolve before it can be filtered out. In

this case the solution should be evaporated approximately to dryness, thus removing nitrates fairly completely.

$$3\,HCl + HNO_3 = Cl_2 + NOCl + 2\,H_2O$$

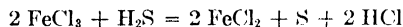
The residue is dissolved in 5 cc. of concentrated HCl and 10–15 cc. of H_2O, then treated in the usual way for precipitation of As^V. Sometimes this difficulty is avoided by reducing the As^V with H_2SO_3 or KI, and precipitating the As^{III} in 0.25 *N* HCl solution. In using an iodide to reduce the As^V it is unnecessary to add excess and boil out the free iodine. If only a few drops are added and the solution then treated with H_2S all of the As will be reduced and precipitated as As_2S_3. This is due to the fact that the I_2 formed in reducing some of the As^V will in turn be converted to I^- again by the H_2S.

$$I_2 + H_2S = S + 2\,HI$$

The iodide, therefore, merely provides a means whereby the As^V is reduced at the expense of some of the H_2S.

11. If As^V is present it must be precipitated completely in Group II otherwise the Group III precipitates may contain arsenates of later group metals (§134, 6, *g*, §183, etc.).

12. The precipitate of sulfides of the arsenic and copper groups must be well washed, otherwise small amounts of later group metals may be present when testing for Group II metals.

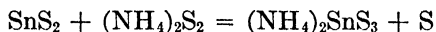
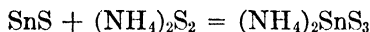
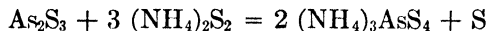
13. When $FeCl_3$ is present in the solution part of the H_2S is oxidized with formation of a white or pale yellow precipitate of free S.

$$2\,FeCl_3 + H_2S = 2\,FeCl_2 + S + 2\,HCl$$

In the absence of Group II metals this sometimes causes slight uncertainty as to whether or not the precipitate is a Group II sulfide. A more serious difficulty is the fact that if Ba is present at the same time the oxidation may be carried somewhat farther, causing loss of Ba by precipitation as $BaSO_4$ in Group II.

§82. **Manipulation.** — After the precipitate has been well washed pierce the point of the filter with a small stirring rod and wash the precipitate into a beaker, using as small an amount of water as possible. If As–div. sulfides are present, add 5 cc. of yellow ammonium sulfide, $(NH_4)_2S_x$, heat to 50–60° (keep well below the boiling point) and let digest for 1–2 minutes.

$$As_2S_3 + 3\,(NH_4)_2S_2 = 2\,(NH_4)_3AsS_4 + S$$

$$SnS + (NH_4)_2S_2 = (NH_4)_2SnS_3$$

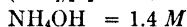
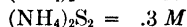
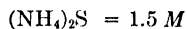
$$SnS_2 + (NH_4)_2S_2 = (NH_4)_2SnS_3 + S$$

Filter, wash once or twice with a small amount of $(NH_4)_2S_x$, and then with hot 1% NH_4NO_3, discarding these washings. The filtrate contains ammonium thio-salts of As, Sb and Sn, which constitute the Arsenic Group (Division A of the second group, §85). The precipitate remaining on the filter contains the sulfides of Hg, Pb, Bi, Cu and Cd which constitute the Copper Group (Division B of the second group, §96).

§83. **Notes.** — 1. Treatment of the Group II precipitate with $(NH_4)_2S_x$ is necessary only when both divisions of the group are present, and is to be avoided when unnecessary. Test a small portion of the precipitate with 1–2 cc. of $(NH_4)_2S_x$. If it dissolves completely, none of the copper group are present so the main precipitate may be treated directly with hot HCl as indicated in §85. If the precipitate does not dissolve completely, filter, and add to the filtrate dilute HCl until it is slightly acid. A milky white precipitate of S will form. If, in addition to this, a bright colored flocculent precipitate

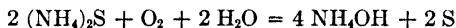
is obtained, metals of the arsenic group are present and the main precipitate must be treated with $(NH_4)_2S_x$. If no bright colored flocculent precipitate forms none of the arsenic group are present, so the main precipitate may be treated directly with HNO_3 as indicated in §96.

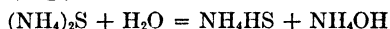
2. Sometimes the amount of precipitate is small and difficult to wash off the filter. In that case place the filter paper carrying the precipitate in the beaker to treat with $(NH_4)_2S_x$.

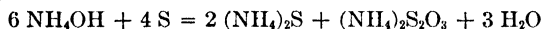
3. The reagent yellow ammonium sulfide is used instead of the colorless ammonium sulfide because the lower sulfides of Sn and Sb (SnS and Sb_2S_3) dissolve readily in the former but not in the latter. This is due to the oxidizing action of the extra sulfur in the $(NH_4)_2S_x$ (like the extra oxygen in H_2O_2), oxidizing SnS and Sb_2S_3 to SnS_2 and Sb_2S_5 which dissolve fairly readily in $(NH_4)_2S$. The reagent should contain sufficient extra sulfur to oxidize the SnS and Sb_2S_3 readily (the maximum used corresponds to the formula $(NH_4)_2S_2$, as shown by the equation $SnS + (NH_4)_2S_2 = (NH_4)_2SnS_3$. It should also supply sufficient S^{--} to dissolve the sulfides readily. For simplicity in writing equations the formula $(NH_4)_2S_2$ is frequently used. The excellent reagent developed experimentally by Curtman and Lehrman[1] has the approximate composition:

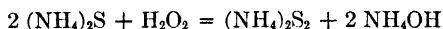
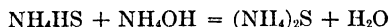
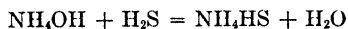
$$(NH_4)_2S = 1.5\,M$$
$$(NH_4)_2S_2 = .3\,M$$
$$NH_4OH = 1.4\,M$$

Ten cc. of this reagent will dissolve 200 mg. of SnS in 1 minute.

Ammonium sulfide is an unsatisfactory reagent even at best because of the readiness with which it oxidizes, e.g.,

$$2\,(NH_4)_2S + O_2 + 2\,H_2O = 4\,NH_4OH + 2\,S$$

and undergoes hydrolysis, e.g.,

$$(NH_4)_2S + H_2O = NH_4HS + NH_4OH$$

Even more complex secondary reactions may occur, e.g.,

$$6\,NH_4OH + 4\,S = 2\,(NH_4)_2S + (NH_4)_2S_2O_3 + 3\,H_2O$$

An old reagent may have a considerable deposit of S in the bottle and have lost all odor of H_2S or NH_4OH. Such a reagent is obviously worthless. For this reason the reagent should be checked up from time to time with a known precipitate of SnS or Sb_2S_3 to see that it will dissolve the precipitate readily. If a satisfactory reagent is not available and only a small amount is needed the following method of preparing it will be found useful. Saturate 5 cc. of 5 *N* NH_4OH with H_2S, keeping the solution cool by placing in a beaker of cold water. Add 5 cc. of 5 *N* NH_4OH and 2–3 cc. of 3% H_2O_2 to the solution.

$$NH_4OH + H_2S = NH_4HS + H_2O$$
$$NH_4HS + NH_4OH = (NH_4)_2S + H_2O$$
$$2\,(NH_4)_2S + H_2O_2 = (NH_4)_2S_2 + 2\,NH_4OH$$

4. Ammonium sulfide is most effective when fairly concentrated, therefore if more than 5–10 cc. of water were used in transferring the precipitate to the beaker most of this should be poured off before adding the reagent.

5. When the precipitate in Group II is large, it is sometimes necessary to use more $(NH_4)_2S_x$ than stated in §82. It is possible to judge if more is needed by letting the precipitate of copper group sulfides settle and noting the color of the clear solution. If it is yellow (best seen against a white background), sufficient reagent has been added; if it is colorless, add 2–3 cc. more of the reagent, let digest 1–2 minutes longer and repeat the observation.

6. Cupric sulfide is slightly soluble in the yellow ammonium sulfide and will give a reddish-brown (occasionally grayish-black) precipitate on acidifying the solution with HCl. It is insoluble in K_2S or Na_2S, which are good solvents for the sulfides of the arsenic group. However, mercuric sulfide is more soluble in the fixed alkali sulfides

[1] Curtman and Lehrman, *J. Ch. Ed.*, **6**, 2203 (1929).

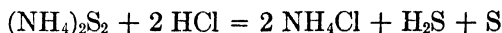
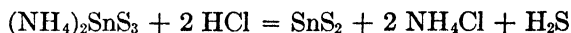
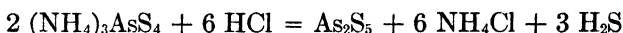
than copper sulfide is in the $(NH_4)_2S_x$. If copper is present and mercury absent, it is sometimes recommended to use K_2S or Na_2S to separate division A from division B in Group II. Some chemists use Na_2S regularly to separate the arsenic group from the copper group, preparing the reagent in such a way that HgS dissolves completely, carrying Hg into the arsenic group.[1] If mercury is present, $(NH_4)_2S_x$ should be used, and separate tests made on the filtrate from Group I for traces of Cu. As a matter of fact, with a satisfactory ammonium sulfide reagent the amount of copper sulfide that dissolves is negligible for ordinary work.

7. On washing the copper group sulfides after separation from the arsenic group by filtration, the wash water frequently turns dark, containing some of the copper group sulfides in suspension. By refiltering and washing with dilute NH_4NO_3 this can usually be remedied.

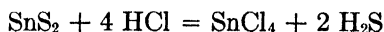
§85. **Manipulation.** — To the filtrate obtained in §82 add diluted HCl (not directly from the reagent bottle), with stirring, until the solution reacts slightly acid. The precipitate will consist of the sulfides of the arsenic group mixed with some sulfur from the excess $(NH_4)_2S_x$.

$$2\ (NH_4)_3AsS_4 + 6\ HCl = As_2S_5 + 6\ NH_4Cl + 3\ H_2S$$

$$(NH_4)_2SnS_3 + 2\ HCl = SnS_2 + 2\ NH_4Cl + H_2S$$

$$(NH_4)_2S_2 + 2\ HCl = 2\ NH_4Cl + H_2S + S$$

Filter, wash several times with hot water, and transfer to a beaker. Add 10 cc. of concentrated HCl, heat to boiling and keep barely at the boiling point for 1–2 minutes. Add 2–3 cc. of water, shake, and filter. As_2S_5 is left practically unattacked while Sb_2S_5 and SnS_2 dissolve fairly readily.

$$Sb_2S_5 + 6\ HCl = 2\ SbCl_3 + 3\ H_2S + 2\ S$$

$$SnS_2 + 4\ HCl = SnCl_4 + 2\ H_2S$$

Wash the precipitate once or twice with HCl, then thoroughly with hot water, and test for As (§87). The filtrate is labelled and set aside to test for Sb and Sn (§89).

§86. Notes. — 1. The process of acidifying the solution should be carried out at a hood rather than in the open laboratory to avoid exposing ones-self and others to the H_2S given off, which not only has an unpleasant odor but is distinctly poisonous.

2. If the acid were poured into the solution directly from the reagent bottle the solution in the reagent bottle would be contaminated with H_2S. The proper manipulation is to pour 3–4 cc. of 5 *N* HCl into a clean test tube, add an equal volume of water, shake, and then add this in small amounts at a time to the solution. Discard any excess not used. If more is needed, rinse the test tube out with distilled water before preparing a fresh mixture.

3. Large excess of HCl is to be avoided since SnS_2 is appreciably soluble in dilute HCl.

4. If none of the arsenic group metals are present a milky white precipitate of S is obtained when the solution is acidified with HCl. The sulfides of the arsenic group are bright colored and flocculent, easily recognizable in contrast to the S even when present in amounts as small as 1 mg.

5. Copper sulfide and HgS are slightly soluble in $(NH_4)_2S_x$, reprecipitating when the solution is acidified. HgS comes down black, but CuS is usually brownish red (liver

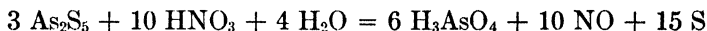
[1] See Noyes, 9th ed. p. 71–2.

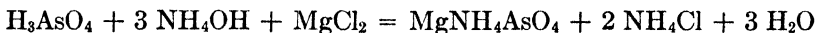
colored), the reddish tinge sometimes causing one to suspect Sb and waste time repeating the tests when the confirmatory test for Sb is negative.

6. After treatment of the precipitate with concentrated HCl it is necessary to dilute slightly with H_2O before filtering because the concentrated HCl would disintegrate the filter paper. Only a slight amount of water should be added, however, or Sb_2S_3 may precipitate.

7. The precipitate of As_2S_5 should be washed first with HCl to avoid reprecipitation of Sb as Sb_2S_3.

§87. **Manipulation.** — Transfer the ppt. of As_2S_5 (+ S) to a beaker, add 5–10 cc. of 5 *N* HNO_3, heat to boiling, and continue the heating for 1–2 minutes after visible evidence of reaction has ceased.

$$3\ As_2S_5 + 10\ HNO_3 + 4\ H_2O = 6\ H_3AsO_4 + 10\ NO + 15\ S$$

Filter, add NH_4OH to the filtrate until distinctly alkaline (2–3 cc. excess), then add 0.5 cc. $MgCl_2$ solution, cool and stir with glass rod to start crystallization. Look for a fine granular precipitate of $MgNH_4AsO_4$.

$$H_3AsO_4 + 3\ NH_4OH + MgCl_2 = MgNH_4AsO_4 + 2\ NH_4Cl + 3\ H_2O$$

§88. **Notes.** — 1. In dissolving the As_2S_5 in HNO_3 the As is sometimes reduced appreciably to As^{III} which does not give the precipitate with $MgCl_2$. Therefore it is necessary to boil the solution a bit longer to reoxidize this As^{III} to As^{V}.

2. Magnesium chloride will give a precipitate of $Mg(OH)_2$, white, with NH_4OH. This is prevented if sufficient NH_4^+ is present in the solution. Ordinarily at this point there is enough HNO_3 to be neutralized by the NH_4OH to take care of this, so no precipitate of $Mg(OH)_2$ is formed if small amounts of $MgCl_2$ are used. If most of the acid was removed by evaporation in the above case it may be desirable to add 3–5 cc. NH_4Cl before treating with $MgCl_2$.

In case of doubt, one can distinguish between $Mg(OH)_2$ and $MgNH_4AsO_4$ by filtering, washing, dissolving the precipitate in 5 *N* HCl and treating the solution with H_2S. If As is present a bright yellow precipitate of As_2S_5 will be obtained.

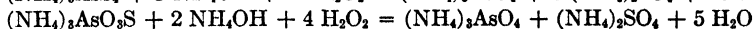
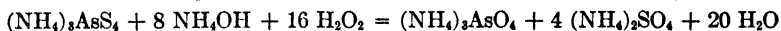
3. Magnesium ammonium arsenate is appreciably soluble in the hot solution, so it is necessary to cool thoroughly in order to get a precipitate with small amounts of As. Further, this compound forms highly supersaturated solutions from which precipitation takes place very slowly. By mechanical means such as (a) stirring the solution with a glass rod so as to scratch the walls of the test tube slightly, or (b) shaking the solution vigorously, or by addition of a few minute particles of the compound itself, this condition of supersaturation can be overcome and the precipitate obtained readily.

4. An alternative test for As: Add to the HNO_3 solution of H_3AsO_4 2–3 cc. of $AgNO_3$, filter if any AgCl ppts., hold test tube in a slanting position and pour in 2–3 cc. of NH_4OH to form an upper layer on the solution. A brown precipitate, Ag_3AsO_4, will form in the neutral zone separating the upper (alkaline) and lower (acid) layers. This test is satisfactory for moderate quantities of As, but is less sensitive than the one above.

5. An alternative method of dissolving As_2S_5: Pour 3–5 cc. of NH_4OH over the precipitate on the filter paper. As_2S_5 dissolves readily.

$$As_2S_5 + 6\ NH_4OH = (NH_4)_3AsS_4 + (NH_4)_3AsO_3S + 3\ H_2O$$

Add to the clear filtrate 3–5 cc. H_2O_2 and boil gently 1–2 minutes. This oxidizes the sulfur in the above compounds to sulfate ion leaving As as AsO_4^{-3}, ready for testing.

$$(NH_4)_3AsS_4 + 8\ NH_4OH + 16\ H_2O_2 = (NH_4)_3AsO_4 + 4\ (NH_4)_2SO_4 + 20\ H_2O$$
$$(NH_4)_3AsO_3S + 2\ NH_4OH + 4\ H_2O_2 = (NH_4)_3AsO_4 + (NH_4)_2SO_4 + 5\ H_2O$$

Add 3–5 cc. NH_4Cl, plus 0.5 cc. $MgCl_2$, cool thoroughly and stir to start precipitation. In this test sometimes a large number of fine bubbles of O_2 (from excess H_2O_2) form as the

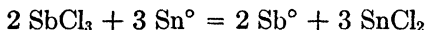
solution is stirred, producing an appearance much like a granular white precipitate. However, this disappears on standing a minute or two (the bubbles rising to the surface and breaking), while a precipitate of $MgNH_4AsO_4$ will persist and even increase in amount.

6. Arsenic is commonly found in solutions as arsenite ion (AsO_3^{-3} or AsO_2^-) and arsenate ion (AsO_4^{-3}). Even in acid solutions the concentrations of As^{+3} and As^{+5} are very small, the As being present largely as molecular H_3AsO_3 and H_3AsO_4. There are many individual tests by which the two valences of As may be distinguished from each other. Most of them, however, are subject to interference by other materials present in the solution. One of the most reliable of the general tests depends on noting how the As precipitates in Group II. If it comes down readily in the dilute acid solution it is in the arsenite form, if it precipitates very slowly in the dilute acid solution, but readily after reduction or after making the solution strongly acid it is in the arsenate form.

7. Arsenic may be separated from Sb and Sn by digesting the sulfides with $(NH_4)_2CO_3$, As_2S_5 dissolves, Sb_2S_5 and SnS_2 do not.

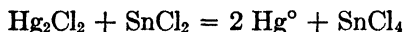
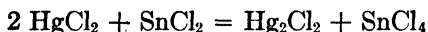
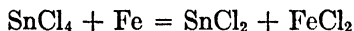
8. Arsenic may also be separated from Sb and Sn by digesting the sulfides with HNO_3 evaporating to dryness, igniting, cooling and extracting with hot water. Arsenic dissolves as H_3AsO_4. Sb and Sn are left as Sb_2O_4 and SnO_2.

§89. **Manipulation.** — Evaporate the filtrate obtained in §85 to 1–2 cc. volume. Test a portion of this solution for Sb as follows: Put 2–3 drops of the solution on the surface of a silver coin that has been cleaned by moistening with HNO_3 and rinsing off. Let stand a minute or two to make sure no dark stain develops from the action of the solution alone. Then drop onto the coin a small inverted V-shaped piece of tin foil so that one end dips into the solution and the other touches the bare coin. If Sb is present a brownish black stain will develop promptly on the surface of the coin.

$$2\,SbCl_3 + 3\,Sn^\circ = 2\,Sb^\circ + 3\,SnCl_2$$

Test the remainder of the solution for Sn as follows: Dilute with water to 5 cc. (approximately) add 1 g. Fe filings, warm until a steady evolution of H_2 takes place, let the reaction continue 3–4 minutes, then filter, letting the filtrate run into a test tube containing 1–2 cc. $HgCl_2$. If Sn is present a white precipitate of Hg_2Cl_2 will form, turning gray if the solution contains any considerable quantity of Sn.

$$SnCl_4 + Fe = SnCl_2 + FeCl_2$$

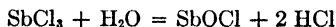
$$2\,HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4$$

$$Hg_2Cl_2 + SnCl_2 = 2\,Hg^\circ + SnCl_4$$

§90. **Notes.** — 1. The filtrate from As_2S_5 contains more or less H_2S, which must be boiled out of the solution, otherwise it will form a black stain on the silver coin, interfering with the test for Sb.

2. The test for Sb is made on only a few drops of the solution. Unless the solution is first evaporated to a small volume the portion tested may contain only a very small fraction of the Sb actually present. The delicacy of the test depends directly on the extent to which the volume of the solution is reduced.

3. The silver coin forms with the tin foil a silver-tin couple which electrolyzes the solution. The current flows from Sn to Ag, causing the Sb to deposit on the surface of the coin.

4. An alternative test, useful for recognizing moderate or larger amounts of Sb, consists in diluting a few drops of the solution to 5–10 cc. with water, obtaining a white, flocculent precipitate of antimony oxychloride.

$$SbCl_3 + H_2O = SbOCl + 2\,HCl$$

Concentrated $SnCl_4$ behaves somewhat similarly.

5. While reducing $SnCl_4$ to $SnCl_2$, Sb forms a black flocculent precipitate of free metal. This is a satisfactory test for moderate quantities of Sb, but cannot be used to identify very small amounts since free carbon, left from the Fe as the latter dissolves, has a similar appearance.

6. Occasionally in moderately acid solution the antimony deposits on the surface of the Fe as a protective coating such that only Sb is exposed. Under these conditions the $SnCl_4$ is reduced so slowly that the ordinary procedure may fail to give a test even with Sn present. It is easy to recognize this condition by the marked decrease in rate of evolution of H_2. If this is observed, continue adding small amounts of Fe filings until the Sb is all reduced and the gas, H_2, comes off smoothly again. Let the reaction continue 2–3 minutes longer, then filter and test as above.

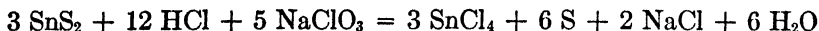
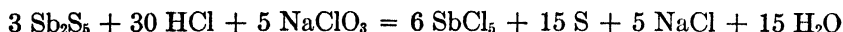
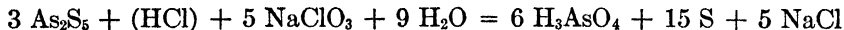
7. The hydroxides of Sn and Sb are insoluble in water, but soluble in strong acids and in strong bases. In the latter, Sn might be present as stannite ion (SnO_2^{--}) or stannate ion (SnO_3^{--}); Sb as antimonite ion (SbO_2^-) or antimonate ion (SbO_4^{-3}). In acid solution Sn would be found as stannous ion (Sn^{++}) or stannic ion (Sn^{+4}); Sb as antimonous ion (Sb^{+3}) or antimonic ion (Sb^{+5}). In HCl solution the Sn and Sb form chlorostannite ($SnCl_4^{--}$), chlorostannate ($SnCl_6^{--}$), chloroantimonite ($SbCl_4^-$), and chloroantimonate ($SbCl_6^-$) ions. Of the different valences of Sn and Sb only Sn^{II} can be easily identified in the original solution, the reaction with $HgCl_2$ in the presence of HCl being characteristic. If Sn^{II} is absent but Sn is found in Group II it must be in solution as Sn^{IV}. Sn^{IV} might be recognized in the solution containing Sn^{II} by reducing a portion of the solution with Fe° in HCl solution and testing with excess of $HgCl_2$, then comparing this with the precipitate obtained by the action of $HgCl_2$ in the presence of HCl directly on an equal portion of the original solution. If the former precipitate is visibly larger than the latter, Sn^{IV} is present. The valence tests for Sb are indirect and generally unsatisfactory. If moderate to strong reducing agents are identified in the solution, report Sb^{III}; if moderate to strong oxidizing agents are identified, report Sb^{V}.

8. Sb may be identified in a mixture of As and Sn by treating the sulfides with HNO_3, evaporating to dryness, adding solid Na_2CO_3 and heating to fusion, then cooling and extracting with cold water. As and Sn will dissolve as Na_3AsO_4 and Na_2SnO_3; Sb will be left as a white precipitate, $Na_2H_2Sb_2O_7$.

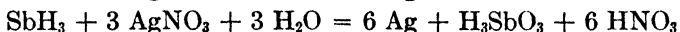
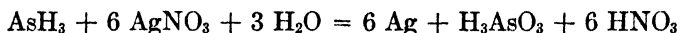
§91. *Alternative Procedures.* — 1. The Marsh test, with its several modifications, constitutes the most accurate method of detecting very small amounts of As and Sb. The following procedure uses the Marsh apparatus and includes a test for Sn: Dissolve the sulfides of As, Sb and Sn in HCl with the aid of small amounts of $NaClO_3$.

$$3\,As_2S_5 + (HCl) + 5\,NaClO_3 + 9\,H_2O = 6\,H_3AsO_4 + 15\,S + 5\,NaCl$$

$$3\,Sb_2S_5 + 30\,HCl + 5\,NaClO_3 = 6\,SbCl_5 + 15\,S + 5\,NaCl + 15\,H_2O$$

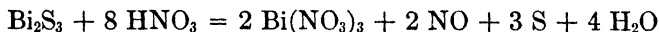
$$3\,SnS_2 + 12\,HCl + 5\,NaClO_3 = 3\,SnCl_4 + 6\,S + 2\,NaCl + 6\,H_2O$$

Boil out any free Cl_2, filter to remove S, transfer to the Marsh apparatus (for details see §69, 6′, *a*), and test the gases evolved for SbH_3 and AsH_3; (1) by heating the hard glass tube and obtaining Sb and As mirrors, (2) by lighting the gases at the outlet tip and holding an evaporating dish in the flame, obtaining spots of metallic Sb and As, and (3) by passing the gases

into $AgNO_3$ solution, filtering, and testing the filtrate for As and the precipitate for Sb (§70, 6, *j*).

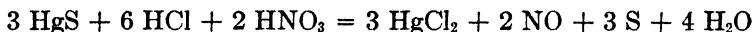
$$AsH_3 + 6\ AgNO_3 + 3\ H_2O = 6\ Ag + H_3AsO_3 + 6\ HNO_3$$
$$SbH_3 + 3\ AgNO_3 + 3\ H_2O = 6\ Ag + H_3SbO_3 + 6\ HNO_3$$

In the Marsh apparatus Sn is reduced to metal. This may be filtered out (along with Sb°, excess of Zn°, etc.), dissolved in HCl to form $SnCl_2$, and identified by testing with $HgCl_2$, with which a white precipitate of Hg_2Cl_2 is formed. The Marsh test is not suited for use by large classes, and should, even with individuals, be used with considerable care; both because of the poisonous nature of AsH_3 and SbH_3, and because of the danger of setting off explosive mixtures of H_2 and air in the apparatus.

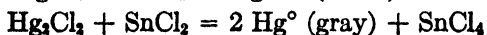
2. By controlling the concentration of HCl it is possible to obtain fairly accurate separations of As, Sb and Sn by successive precipitation of the sulfides. Precipitate As_2S_5 in the presence of 10 *N* HCl (concentrated HCl diluted $\frac{1}{6}$ with H_2O), filter and wash with 10 *N* HCl. Dilute the filtrate to three times its volume with water and treat with H_2S, precipitating Sb_2S_3. Filter and wash. Add NH_4OH to filtrate till nearly neutral, then treat with H_2S, precipitating SnS_2; or evaporate the solution to a small volume and apply other tests for Sn.

§96. **Manipulation.** — Transfer the precipitate (§82) containing the sulfides of the copper group to a beaker or casserole, decant any excess of water used in this process, add 5–8 cc. of water and an equal volume of 5 *N* HNO_3, heat to boiling, and keep just at the boiling point for 1–2 minutes. Mercuric sulfide is unattacked (§58, 6, *e*) and remains as a black precipitate, but the sulfides of Pb, Bi, Cu and Cd dissolve.

$$Bi_2S_3 + 8\ HNO_3 = 2\ Bi(NO_3)_3 + 2\ NO + 3\ S + 4\ H_2O$$
$$3\ CdS + 8\ HNO_3 = 3\ Cd(NO_3)_2 + 2\ NO + 3\ S + 4\ H_2O$$

Filter and wash, catching the filtrate in a casserole and setting it aside to test for Pb, Bi, Cu and Cd (§98).

Transfer the precipitate to a casserole, add 6–8 cc. of HCl and 2–3 cc. of HNO_3, heat to boiling, and keep at the boiling point until the reaction appears to be complete.

$$3\ HgS + 6\ HCl + 2\ HNO_3 = 3\ HgCl_2 + 2\ NO + 3\ S + 4\ H_2O$$

Filter, boil out any free Cl_2, cool and test for Hg by adding 4–5 cc. of $SnCl_2$. If Hg is present a white precipitate will form, turning dark gray if the amount is small.

$$2\ HgCl_2 + SnCl_2 = Hg_2Cl_2\ \text{(white)} + SnCl_4$$
$$Hg_2Cl_2 + SnCl_2 = 2\ Hg°\ \text{(gray)} + SnCl_4$$

§97. Notes. — 1. HNO_3 reacts slowly enough with some of the sulfides so that it is necessary to digest the precipitate with the reagent rather than attempting to extract these by pouring the reagent repeatedly over the precipitate on the filter.

2. The separation of Hg from the other metals of the copper group by differential action of HNO_3 on the sulfides requires reasonable control of the concentration of the HNO_3. If this falls much below 2 *N* the reaction with the soluble sulfides is unsatisfactory, if it becomes much higher than 5 *N* the HgS is attacked appreciably. Since the concentration is increased by evaporation during the boiling it is desirable to start with not higher than 2–2.5 *N* HNO_3.

3. A few drops of $NaNO_2$ may be added to hasten the reaction of HNO_3 with the soluble sulfides without dissolving HgS.

4. The S formed from Bi_2S_3, etc., usually appears first in the dark, spongy, amorphous form. On further heating it changes to the light yellow, crystalline modification. With a little experience it will not be mistaken for HgS and can be discarded unless one is looking for small amounts of Hg. The S may be further identified by lifting it out with a glass rod, rinsing, and burning in the flame, noting that it burns completely, with a blue flame, and with a characteristic suffocating odor.

5. Sb and Sn, incompletely separated from the copper group (failure to use sufficient $(NH_4)_2S_x$, unsatisfactory reagent, incomplete washing, etc.), will be converted by the HNO_3 to white precipitates, H_3SbO_4 and H_2SnO_3.

6. Sometimes, from use of too concentrated HNO_3 or too long continued treatment with this reagent, the black HgS is converted to white, granular $Hg(NO_3)_2 \cdot 2HgS$. This will respond to the usual test for Hg, which should not be omitted because the residue is gray or white instead of black. When this effect is obtained small amounts of the Hg may dissolve, interfering partially with the tests for Bi and Cd.

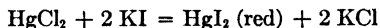
7. If Hg is incompletely converted to HgS at the beginning of Group II (§81, 7), it may dissolve more or less completely in the dilute HNO_3, thus losing the test for Hg and causing trouble in the tests for Bi and Cd.

8. In attempting to remove Cl_2 before testing for Hg it must be remembered that $HgCl_2$ is appreciably volatile, so the solution cannot be boiled to dryness without serious loss of Hg. A safer procedure consists in adding 5–10 cc. of water and then boiling for only 1–2 minutes.

9. In testing for Hg with $SnCl_2$ it is necessary to add sufficient reagent so that only part of it will be oxidized by the small amount of Cl_2 still present.

10. Alternative test for Hg: Add to the solution a small piece of bright metallic copper, warm slightly and let stand 2–3 minutes. Hg is displaced by the Cu°, forming an amalgam on the surface of the latter. With a small amount of Hg present a lustrous silvery coating becomes visible on the Cu; with larger amounts this may appear duller and gray due to fine drops of Hg°. On polishing with a dry cloth these latter disappear and the shiny surface is obtained.

11. Alternative test for Hg: Add to the $HgCl_2$ solution barely enough KI to redissolve the precipitate first formed:

$$HgCl_2 + 2\,KI = HgI_2\text{ (red)} + 2\,KCl$$
$$HgI_2 + 2\,KI = K_2HgI_4$$

Add NaOH till strongly alkaline, then a few drops of NH_4OH, looking for a red-brown precipitate (tan color if the amount of Hg is small).

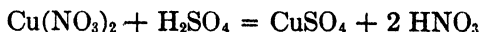
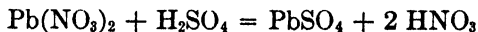
$$NH_4OH + 2\,K_2HgI_4 + 3\,NaOH = OHg_2NH_2I + 4\,KI + 3\,NaI + 3\,H_2O$$

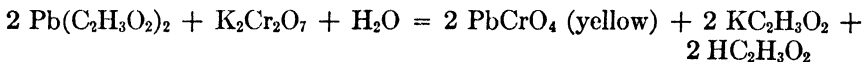
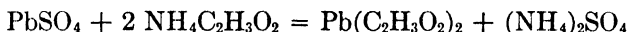
12. Mercury may be detected in all its compounds by ignition in a hard glass tube with fusion mixture ($Na_2CO_3 + K_2CO_3$) (§58, 7). Free mercury forms a sublimate (shiny or gray) in the upper part of the tube. Cool, place in horizontal position, add a few drops of HNO_3 and a small crystal of KI. On warming, the I_2 sublimes and combines with the Hg forming the scarlet red HgI_2.

13. Mercury is found in solution in the bivalent form chiefly as Hg^{++}. In the presence of Cl^- the mercury will be largely undissociated $HgCl_2$ or the complex ion $HgCl_4^{--}$.

§98. Manipulation. — To the filtrate (§96), containing the nitrates of Pb, Bi, Cu and Cd, add 2–3 cc. of concentrated H_2SO_4 and evaporate

cautiously (at the hood) until dense white fumes from decomposition of H_2SO_4 appear.

$$Pb(NO_3)_2 + H_2SO_4 = PbSO_4 + 2\ HNO_3$$
$$Cu(NO_3)_2 + H_2SO_4 = CuSO_4 + 2\ HNO_3$$

Cool thoroughly, add 15–20 cc. of H_2O, warm slightly and let stand 1–2 minutes. Stir the solution vigorously and pour quickly into a small beaker, let stand 1–2 minutes for any $PbSO_4$ to settle, then swirl gently and set on a dark surface watching for a finely divided white precipitate that may collect in the center of the beaker. Filter and wash, setting the filtrate aside to test for Bi, Cu and Cd (§100). Dissolve the precipitate in 5 cc. of 2.5 *N* $NH_4C_2H_3O_2$ and add a few drops of $K_2Cr_2O_7$.

$$PbSO_4 + 2\ NH_4C_2H_3O_2 = Pb(C_2H_3O_2)_2 + (NH_4)_2SO_4$$
$$2\ Pb(C_2H_3O_2)_2 + K_2Cr_2O_7 + H_2O = 2\ PbCrO_4\ \text{(yellow)} + 2\ KC_2H_3O_2 + 2\ HC_2H_3O_2$$

§99. **Notes.** — 1. Occasionally Ag, present in small amounts, escapes precipitation in Group I (§63, 4, 6). In such cases it precipitates in Group II as Ag_2S, insoluble in $(NH_4)_2S_x$, but soluble in dilute HNO_3. The proper place to test for it in Group II is immediately before adding H_2SO_4. Add a few drops of HCl. If a curdy white precipitate forms add more HCl until precipitation is complete; filter, wash, and apply confirmatory test by dissolving in NH_4OH and reprecipitating with HNO_3.

2. Lead sulfate is appreciably soluble in HNO_3, therefore it is necessary to remove the latter in order to obtain satisfactory precipitation of $PbSO_4$. Nitric acid boils out of the solution at a temperature of 120–130°, while H_2SO_4 does not fume appreciably until a temperature of 180–200° is reached. Therefore HNO_3 can be removed by evaporating until fumes of H_2SO_4 are recognized. In the process of evaporation 3 stages may be noted: (1) chiefly steam, which condenses and then re-evaporates as it rises from the casserole, (2) largely HNO_3, which forms slightly denser clouds with strong sour taste, changing also to invisible gases on dilution with air, and (3) when the solution is reduced in volume to 3–4 cc., the HNO_3 fumes disappear, then on stronger heating much denser white clouds of smoke rise from the solution. These have a marked choking effect when breathed, causing one to check breathing and to cough. Also, they do not evaporate and disappear in the air.

3. Since the acid fumes are hard on books, clothes, etc., and the H_2SO_4 fumes in particular are very disagreeable, the evaporation should be carried out in a hood having adequate draft. Further, since the H_2SO_4 fumes serve merely to indicate that the HNO_3 has been removed the reaction should be stopped as soon as these fumes are definitely recognized. Then let the solution cool until it no longer fumes before taking it back to the laboratory desk.

4. It is desirable to use a moderate excess of H_2SO_4 in this process for two reasons: (1) to reduce the solubility of $PbSO_4$ sufficiently so that it will precipitate with reasonable completeness and (2) to prevent possible hydrolysis of the $Bi_2(SO_4)_3$ with precipitation of $Bi_2O_2SO_4$ when the solution is diluted with water. Concentrated H_2SO_4 is approximately 36 *N*. If not more than 1 cc. of the concentrated acid is used up in forming sulfates of the metals and by decomposition, the solution after dilution to 20 cc. with water will be approximately 1.8 *N* with respect to H_2SO_4 if 2 cc. of concentrated H_2SO_4 was used at the start. This is ample for the purposes indicated.

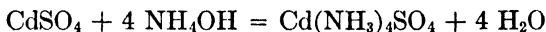
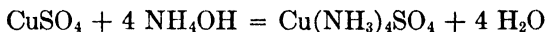
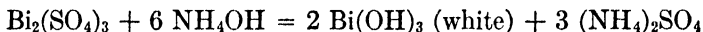
5. Bismuth sulfate and $CuSO_4$ are only slightly soluble in concentrated sulfuric acid. If these metals are present in moderate amounts they form coarse granular precipitates, white or light gray in color, when the H_2O and HNO_3 are removed by evaporation. They dissolve fairly promptly when the solution is diluted with water. Lead sulfate on the other hand, is relatively insoluble in dilute H_2SO_4, but slightly soluble in concen-

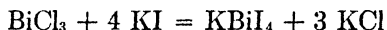
trated H_2SO_4 [forming an acid sulfate, $Pb(HSO_4)_2$]. With small amounts of Pb, therefore, no precipitate may form until after dilution with water.

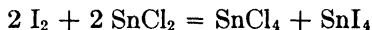
6. Alternative test for Pb: Wash the precipitate of $PbSO_4$ in the beaker several times by decantation (pour off the solution, add 5 cc. of H_2O to the ppt., stir, let settle, then pour off the water, repeating several times). Then add a few drops of KI, which changes part of the white precipitate to yellow PbI_2. KI cannot be substituted for $K_2Cr_2O_7$ to test for Pb in the $NH_4C_2H_3O_2$ solution (see p. 159, footnote 1).

7. Lead found in Group II forms the same ions in the original solution as lead found in Group I (§65, 8).

§100. Manipulation. — To the filtrate from $PbSO_4$ (§98), add NH_4OH, 2–3 cc. at a time, with stirring, until the solution is distinctly alkaline.

$$Bi_2(SO_4)_3 + 6\ NH_4OH = 2\ Bi(OH)_3\ \text{(white)} + 3\ (NH_4)_2SO_4$$
$$CuSO_4 + 4\ NH_4OH = Cu(NH_3)_4SO_4 + 4\ H_2O$$
$$CdSO_4 + 4\ NH_4OH = Cd(NH_3)_4SO_4 + 4\ H_2O$$

Filter, wash thoroughly, and set filtrate aside to test for Cu and Cd (§102). Dissolve the precipitate in 4–5 cc. HCl and add 1–2 cc. KI. Bismuth forms a yellow (tan to reddish brown in higher concentrations) colored solution of potassium bismuth iodide, $KBiI_4$.

$$BiCl_3 + 4\ KI = KBiI_4 + 3\ KCl$$

If color develops add a few drops of $SnCl_2$ to remove any color due to free I_2.

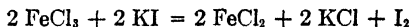
$$2\ I_2 + 2\ SnCl_2 = SnCl_4 + SnI_4$$

If the color remains Bi is present.

§101. Notes. — 1. The use of excessive amounts of H_2SO_4 in precipitating $PbSO_4$ may cause unnecessary dilution of the solution and waste of reagent when neutralizing with NH_4OH. Concentrated H_2SO_4 is 35–36 N, while reagent NH_4OH is 5 N, so for each unnecessary cubic centimeter of acid added there will be used up 7 cc. of NH_4OH.

2. From inaccuracy in earlier separations it is possible to obtain precipitates with NH_4OH without Bi being present. Thus, failure to redissolve Group III hydroxides before precipitating Group II, or failure to wash the Group II precipitate adequately may cause precipitation of $Fe(OH)_3$, $Cr(OH)_3$ or $Al(OH)_3$ where $Bi(OH)_3$ is expected. Mercury (§97, 6, 7) and Pb (§99, 2) are sometimes present in sufficient amounts to form white precipitates ($Hg_2(NH_2)_2SO_4$, $Pb_2(OH)_2SO_4$) with the NH_4OH. These do not interfere with the confirmatory test for Bi given above.

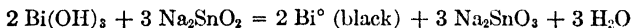
3. When Cu is present in considerable amounts the deep blue color of the $Cu(NH_3)_4^{++}$ makes it difficult to recognize small amounts of $Bi(OH)_3$. Usually, if Bi is present, the solution will appear slightly cloudy instead of clear blue. In case of doubt it is safer to filter, wash thoroughly, and try a confirmatory test for Bi.

4. Free I_2 may be formed when KI is added to test for Bi, due to the presence of oxidizing agents such as $FeCl_3$ (see 2 above) and $CuCl_2$ (incomplete washing of $Bi(OH)_3$ before applying test).

$$2\ FeCl_3 + 2\ KI = 2\ FeCl_2 + 2\ KCl + I_2$$
$$2\ CuCl_2 + 2\ KI = Cu_2Cl_2 + 2\ KCl + I_2$$

Since the color of an iodine solution is much like that of BiI_4^-, the iodine color must be destroyed before the test for Bi is certain. In adding $SnCl_2$ to take care of this, do not use

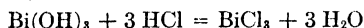
excessive quantities of the reagent (1 cc. $SnCl_2$ will decolorize a moderate amount of I_2) or the decrease in depth of color resulting from dilution of BiI_4^- may be mistaken for removal of color by reduction of I_2.

5. Alternative test for Bi: Prepare a solution of Na_2SnO_2 by adding NaOH to 2 cc. of $SnCl_2$ until the precipitate of $Sn(OH)_2$ is barely dissolved in excess of NaOH, then pour this over the precipitate of $Bi(OH)_3$ on the filter paper. If Bi is present the precipitate turns black.

$$2\,Bi(OH)_3 + 3\,Na_2SnO_2 = 2\,Bi^\circ\text{ (black)} + 3\,Na_2SnO_3 + 3\,H_2O$$

This is a fairly delicate test for Bi, but is less characteristic than the KI test since a number of metals (Hg, Pb, etc.) are reduced to the free state by Na_2SnO_2. It may be used as an additional confirmatory test after the BiI_4^- color is obtained by adding NaOH to the latter solution till alkaline and then adding Na_2SnO_2.

6. Alternative test for Bi: The precipitate of $Bi(OH)_3$ may be dissolved in HCl and the solution evaporated nearly to dryness and then diluted to 15–20 cc. with water.

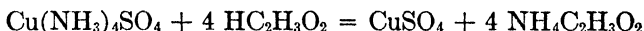
$$Bi(OH)_3 + 3\,HCl = BiCl_3 + 3\,H_2O$$

$$BiCl_3 + H_2O = BiOCl\text{ (white)} + 2\,HCl$$

This test is satisfactory for recognizing moderate amounts of Bi, but is less delicate than either of the others.

7. Bismuth is found in solution in the form of Bi^{+3}, though in the presence of Cl^- this forms complex ions, $BiCl_4^-$ and $BiCl_5^{--}$.

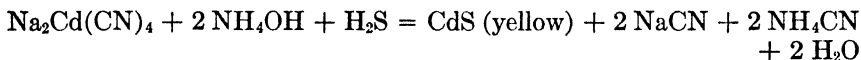
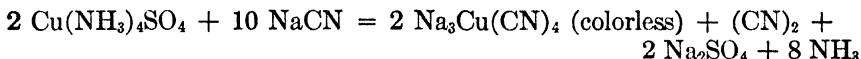
§102. **Manipulation.** — Note the color of the filtrate from the $Bi(OH)_3$ (§100). If it is deep blue, copper is present in moderate amounts. If the color is faint or uncertain take 5–10 cc. of the solution, acidify with acetic acid, and add a few drops of $K_4Fe(CN)_6$.

$$Cu(NH_3)_4SO_4 + 4\,HC_2H_3O_2 = CuSO_4 + 4\,NH_4C_2H_3O_2$$

$$2\,CuSO_4 + K_4Fe(CN)_6 = Cu_2Fe(CN)_6\text{ (red brown)} + 2\,K_2SO_4$$

To test for Cd if Cu is present, add to the ammoniacal solution NaCN, 1–2 cc. at a time until the solution is colorless, then 1–2 cc. excess, and pass in H_2S.

$$2\,Cu(NH_3)_4SO_4 + 10\,NaCN = 2\,Na_3Cu(CN)_4\text{ (colorless)} + (CN)_2 + 2\,Na_2SO_4 + 8\,NH_3$$

$$Cd(NH_3)_4SO_4 + 4\,NaCN = Na_2Cd(CN)_4 + Na_2SO_4 + 4\,NH_3$$

$$Na_2Cd(CN)_4 + 2\,NH_4OH + H_2S = CdS\text{ (yellow)} + 2\,NaCN + 2\,NH_4CN + 2\,H_2O$$

If Cu is absent pass in H_2S directly.

$$Cd(NH_3)_4SO_4 + H_2S = CdS + (NH_4)_2SO_4 + 2\,NH_3$$

§103. Notes. — 1. If Ni is not properly retained in the filtrate from Group II it may give a blue color when NH_4OH is added. In such a case the $K_4Fe(CN)_6$ test will distinguish Cu from Ni, the latter forming a greenish-white precipitate in the presence of which the red brown $Cu_2Fe(CN)_6$ would be readily distinguished.

2. Precipitation with $K_4Fe(CN)_6$ is a more delicate test for Cu^{++} than production of blue color with NH_4OH. With very small amounts of Cu the precipitate may remain suspended, imparting a pink to rose color to the solution.

3. Cadmium forms a white precipitate with $K_4Fe(CN)_6$, but the red color of the $Cu_2Fe(CN)_6$ makes the latter easy to recognize if Cu is present.

4. The effect of the NaCN is to remove Cu^{++} (and Cu_2^{++}) from the solution to a sufficient extent so that no precipitate of CuS (or Cu_2S) will form when H_2S is passed into the solution. Cupric-ammonia ion undergoes sufficient dissociation so that it reacts readily with H_2S, while $Cu(CN)_4^{-3}$ does not. Since the former is blue while the latter is colorless it is possible to tell, by the loss of color, when the former is effectively converted to the latter. However, with moderate amounts of Cu present a solution which is barely decolorized may still form some CuS with H_2S, so a slight excess of NaCN is necessary. In the case of Cd, the NaCN still leaves Cd^{++} in solution in sufficient concentration to react effectively with the H_2S.

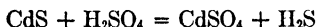
5. When Cu is present in moderate amounts the solution turns yellow on treatment with H_2S, due to the formation of $C_2S_2(NH_2)_2$.

$$(CN)_2 + 2\,H_2S = C_2S_2(NH_2)_2$$

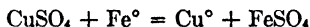
This should not be mistaken for CdS which separates as a precipitate, producing a cloudy effect even with very small amounts of Cd.

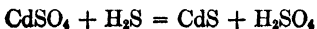
6. In alkaline solution CdS sometimes precipitates in a greenish-yellow modification instead of the usual bright yellow form. The former can be converted to the latter if desired by filtering, washing, dissolving in HNO_3 and reprecipitating with H_2S after adding NH_4OH till the solution is nearly neutral.

7. Occasionally a black precipitate is obtained in the test for Cd. Failure to carry out earlier procedures properly may let any of the other metals of the copper group stay in solution and precipitate with H_2S where CdS is expected. In such a case the analysis should be repeated to make sure none of the other metals have been overlooked, but it is possible to examine the black precipitate fairly directly for Cd. Filter, wash thoroughly, transfer to a casserole, add 10 cc. of H_2O and 2 cc. of concentrated H_2SO_4, heat to boiling, and let stand about 1 minute. The other sulfides do not dissolve but CdS does.

$$CdS + H_2SO_4 = CdSO_4 + H_2S$$

Filter, nearly neutralize with NH_4OH, and pass in H_2S, obtaining a yellow precipitate of CdS if Cd is present. This procedure may be used directly on the precipitate at the beginning of the analysis of the copper group if Cd is the only metal one wishes to identify. It is possible to use this method to test for Cd when Cu is present. Precipitate both CuS and CdS by treating the ammoniacal solution with H_2S. Filter and test as above for Cd.

8. Alternative test for Cd when Cu is present: acidify the solution with H_2SO_4 adding about 1 cc. excess of the concentrated acid. Add about 1 g. of iron filings or powdered iron (this must be finely divided for satisfactory results), warm sufficiently to obtain ready evolution of H_2, and shake moderately for about 2 minutes. Copper is precipitated as the free metal, while Cd stays in solution.

$$CuSO_4 + Fe^\circ = Cu^\circ + FeSO_4$$

Filter, nearly neutralize the filtrate with NH_4OH, and pass in H_2S:

$$CdSO_4 + H_2S = CdS + H_2SO_4$$

REACTIONS OF SALTS OF PLATINUM METALS[1]

	Ruthenium ($RuCl_3$).	Rhodium ($RhCl_3$).	Palladium ($PdCl_2$).	Osmium ($OsCl_4$).	Iridium ($IrCl_4$).	Platinum ($PtCl_4$).
Colour[2]	Dark brown	Red	Brownish yellow	Yellow	Dark brown	Yellow
Hydrogen[2] sulphide at 80° C.	Azure-blue color on prolonged treatment	Brownish black ppte., Rh_2S_3	Brownish black ppte., PdS	Brownish black ppte., OsS_4	Brownish black ppte., Ir_2S_3	Brownish black ppte., PtS_2
Ammonium sulphide	Dark brown ppte., Ru, difficultly soluble in excess	Dark brown ppte., Rh_2S_3, insoluble in excess	Black ppte., PdS, insoluble in excess	Dark ppte., insol. in excess	Brown ppte., Ir_2S_3, soluble in excess	Brown ppte., PtS_2, soluble in excess to $(NH_4)_2PtS_3$
Caustic alkalies	Black ppte. of hydrated oxide insoluble in excess	Yellow-brown ppte., $Rh(OH)_3$, soluble in excess	Yellowish brown basic salts soluble in excess	Brownish red $OsO_2.2H_2O$	Green solution Brownish black double chloride ppted.	Dark ppte. of $PtO_2.xH_2O$
Ammonium[2] hydroxide on warming	Greenish coloring	Slow decolorization	Decolorized	Yellowish brown ppte.	Bright color	Slow decolorization
Saturated[2] NH_4Cl solution	Brown ppte.	No ppte.	No ppte.	Red ppte.	Black ppte.	Yellow ppte., $(NH_4)_2PtCl_6$
Saturated KCl solution	Violet cryst. ppte. of K_2RuCl_5	Red cryst. ppte., K_2RhCl_5	Red ppte. of K_2PdCl_4	Brown cryst. ppte., K_2OsCl_6	Brownish red ppte. of K_2IrCl_6	—
KI solution[2] (1 : 1000)	No change	No change	Dark ppte.	No change	Yellow color	Slow red-brown color
$Hg(CN)_2$ solution	No change	No change	White ppte., $Pd(CN)_2$	No change	No change	No change
KCNS, 1 per cent. solution	Dark violet color	Yellow color	Unchanged	Unchanged	Decolorized	Increased yellow color
Hydrazine in hydrochloric[2] acid solution	Yellow color	Yellow color	Black ppte., metallic Pd	No change	Yellow color	Black ppte., metallic Pt
Dimethyl[2] glyoxime	Yellow ppte.	No change	No change	No change	No change	No change
Metallic zinc	Ppte., Ru	Ppte., Rh	Ppte., Pd	Ppte., Os	Ppte., Ir	Ppte., Pt

[1] Friend, IX, Pt. 1, p. 332.
[2] With the platinum-metal salts in dilute solution. Based on the results of Mylius and Mazzucchelli, Zeitsch. anorg. Chem., **1914**, 89, I.

RARER METALS OF THE SECOND GROUP

RUTHENIUM, RHODIUM, PALLADIUM, IRIDIUM, OSMIUM, TUNGSTEN, RHENIUM, GERMANIUM, TELLURIUM, SELENIUM

§104. Ruthenium (*Ruthenia* = Russia). Ru = 101.7. Atomic No. 44. Valence 2, 3, 4, 6, 7 and 8. Discovered by Claus in 1845.

1. Physical Properties. — Density, 12.304 at 19°;[1] melting point, 2450°;[2] boiling point, > 2700°. Next to osmium, ruthenium is the most difficultly fusible of all the platinum metals. In compact form, Ru resembles Pt, though Ru is somewhat harder and more brittle. Powdered Ru is a very good catalyst in certain reactions. Explosive Ru can be prepared by dissolving its Zn alloy in HCl. The Zn goes into solution, leaving a finely divided residue of Ru. There is practically no commercial demand for the metal.

2. Occurrence. — Ruthenium is found in crude, native platinum to the extent of about 0.5%–2%. In 1929 Ru was quoted at $40–$50 per ounce.

3. Preparation. — Ruthenium is obtained as a by-product in the refining of platinum (§74, 3), from the natural alloy, osmiridium, accompanying the platinum. The alloy is "dissolved" in molten zinc, the cooled product treated with aqua regia and the solution distilled. The distillate contains the osmium. Iridium is next removed as ammonium chloroiridate, leaving rhodium and ruthenium to be precipitated with Zn, fused with KOH and KNO_3 and finally separated by extracting the potassium ruthenate with water, leaving the rhodium in the residue. The extract is acidified, RuO_4 precipitated and ignited to the metal. Another method, advocated by Noyes and Bray,[3] is distinctly shorter. Evaporation with HNO_3 removes the osmium. The residue is treated with HNO_3 and $HClO_4$, then heated to fumes of $HClO_4$, whereupon the ruthenium distils over as RuO_4. It is absorbed in NaOH, precipitated as the oxide, and converted to the metal.

4. Oxides and Hydroxides. — Ruthenium monoxide, RuO, apparently has not been prepared. The trioxide, RuO_3, and heptoxide, Ru_2O_7, are believed to exist in certain combinations. Ruthenium dioxide, RuO_2, may be obtained by heating the finely powdered metal[4] above 600°. It sublimes, forming green iridescent crystals. Ruthenium tetroxide,[5] RuO_4, is obtained by distillation with HNO_3 and $HClO_4$ at the boiling point (see above). It is a golden yellow, crystalline powder, having a peculiar odor, somewhat like ozone. Its aqueous solutions are weakly acid and form salts, e.g., $(NH_4)_2RuO_5$.[6] It melts at 25.5° and decomposes at about 106°, forming RuO_2.[7] The hydroxides, $Ru(OH)_2$, $Ru(OH)_3$ and $Ru(OH)_4$ have been reported as precipitating upon addition of a fixed alkali hydroxide to the corresponding chloride. The existence of the first has been questioned; the second and third are believed to be hydrated oxides, $Ru_2O_3 \cdot 3H_2O$ and $RuO_2 \cdot xH_2O$, respectively.[8]

[1] Ruff and Vidic, *Z. anorg. allgem. Ch.*, **143**, 171 (1925).

[2] I. C. T.

[3] Noyes and Bray, p. 17. It is realized, of course, that methods for recovery and purification of the platinum metals are analytical procedures, quantitative if available, on a large scale.

[4] Gutbier, *et al.*, *Z. anorg. allgem. Ch.*, **96**, 182 (1916).

[5] *Idem.*

[6] Krauss, *Ibid.*, **119**, 217 (1921).

[7] Wöhler, *et al.*, *Ibid.*, **139**, 205–19 (1924), *C.A.* **19**, **790**, state that the anhydrous oxides, RuO_2 and RuO_4, and the hydrated oxides of Ru^{+4}, Ru^{+3} and Ru^{+2} are all stable. The last two undergo auto-oxidation to RuO_2 and Ru°. Cf. Krauss and Schrader, *Ibid.*, **176**, 385–97 (1928), *C.A.* **23**, 1073.

[8] Gutbier and Ransohoff, *Z. anorg. allgem. Ch.*, **45**, 243 (1905).

5. Solubilities. — Ruthenium is difficultly soluble in aqua regia, insoluble upon fusion in $K_2S_2O_7$, but soluble upon fusion in $NaOH + NaNO_3$. The oxides Ru_2O_3 and RuO_4 are slightly soluble in H_2O; RuO_2 is readily soluble. The tetroxide is readily soluble in NaOH, from which alcohol precipitates the metal.

6. Reactions. — The alkalis precipitate from ruthenic chloride, $RuCl_3$, the dark yellow hydroxide, soluble in acids, insoluble in the fixed alkalis, soluble in NH_4OH, giving a greenish-brown liquid. H_2S slowly precipitates the black sulfide (formed at once by $(NH_4)_2S$), the solution becoming blue due to reduction to Ru^{++}.[1] The sulfide is insoluble in alkali sulfides. KI gives, with hot solutions, a black precipitate of ruthenic iodide. KCNS forms, after some time in the cold, a red color, which, upon heating, becomes a beautiful violet. This reaction is characteristic of Ru. The double nitrites are soluble, and if to the solution $(NH_4)_2S$ is added, a characteristic crimson liquid is obtained. Upon standing, a brown precipitate separates. Zn°, Mg°, or Al° at first reduces the Ru^{+4} to Ru^{++}, blue, then to Ru°. Molecular hydrogen also reduces ions of Ru to the metal.

7. Ignition. — If Ru° is heated to 600° or higher, a sublimate of RuO_2 is obtained. The tetroxide, RuO_4, decomposes at 106° to give the dioxide.

8. Detection. — *a.* As indicated above, Ru is separated from the other platinum group metals (except osmium) by distillation.[2] The distillate, collected in NaOH, gives an orange to red solution of RuO_5^{--} which is reduced to the black oxide, Ru_2O_3, upon addition of alcohol. Osmium does not interfere.

b. Ruthenium solutions, heated with thiourea and HCl (d. 1.2), give a blue color. The test is sensitive to 0.003 mg. of Ru per cubic centimeter. Thiocarbanilide, used in place of thiourea, produces a blue green color. The test becomes 10 times as delicate by extraction with ether.

9. Determination. — Ruthenium may be separated as the tetroxide by distillation, converted to the metal and weighed as such.[3,4] *Volumetrically*, Ru may be determined by titration of H_2RuCl_6 in strong HCl solution with $SnCl_2$. An excess of the standard solution is added and the excess determined with iodine.[5] Results are slightly low with this method.

10. Oxidation and Reduction. — RuO_4, treated with HCl, becomes H_2RuCl_6, which with $SnCl_2$ gives H_2RuCl_5. Ru^{+8-x} is changed to RuO_4 by distillation with $KClO_3$ and HCl, or HNO_3 and $HClO_4$. RuO_4 decomposes on heating to RuO_2. Zn° reduces Ru ions to Ru^{++}, deep blue, and finally to the metal, Ru°.

§105. Rhodium (Gr. *rhodon* = rose).[6] Rh = 102.91. Atomic No. 45. Valence 3 and 4. Discovered by Wollaston in 1804.

1. Physical Properties. — Density, 12.472;[7] melting point, 1950°;[8] boiling point, $>2500°$. Rhodium is a silvery white metal, nearly as ductile and malleable as silver. Like other members of the platinum group, Rh° precipitated by alcohol or formic acid, appears as a black, spongy mass. The chief use of Rh is to alloy with Pt, the product being harder and more durable than Pt alone.

2. Occurrence. — Rhodium is found in the platinum ores to the extent of 0.5%–2%.[9] In 1929 the price ranged from $40 to $55 per ounce.

[1] Cf. Remy, *Z. angew. Ch.*, **42**, 289–90 (1929), *C.A.* **23**, 4902; Gall, *Z. angew. Ch.*, **41**, 1070–1 (1928).

[2] Cf. Orlow, *Ch. Ztg.*, **32**, 77 (1908); *C.A.* **2**, 971.

[3] Hillebrand and Lundell, p. 280, 291.

[4] Cf. Howe, Howe and Ogburn, *J. Am. Ch. Soc.*, **46**, 335 (1924).

[5] Howe, *Science*, **65**, 503 (1927), *C.A.* **21**, 2441; *J. Am. Ch. Soc.*, **49**, 2393 (1927).

[6] The color of aqueous solutions of Rh salts.

[7] Rose, *J. Inst. Metals*, **33**, 109–14 (1925).

[8] B. Stds. Cir. 35.

[9] Cf. Friend, IX, 1, p. 257.

3. Preparation. — The ore is washed to remove the " sand " and the crude metal thus secured is refined, primarily to obtain the Pt. Rhodium may be considered a by-product of the process. Several methods are available for its recovery. After the removal of Os, Ru and Pd, the remaining Rh, Ir and Pt may be treated with $BaCO_3$ to precipitate Rh and Ir hydroxides. The process is repeated two or three times to remove all Pt. Finally the Rh is separated from Ir by reduction of the former to Rh° with Ti^{+3}. The resulting product will contain some Ir which is very difficult to remove.[1]

4. Oxides and Hydroxides. — Two oxides have been fairly well identified: Rh_2O_3 and RhO_2. The former is obtained when metallic Rh is heated in air below 1150°.[2] The action is reversed at higher temperatures. The corresponding hydroxide, $Rh(OH)_3$, yellow, precipitates when Rh^{+3} is treated with a fixed alkali hydroxide. Rhodium dioxide, RhO_2, is formed when Rh° is fused with NaOH and KNO_3. It is a brown powder, insoluble in acids or alkalis.

5. Solubilities. — Metallic rhodium or an alloy with Au is almost insoluble in acids, including aqua regia. Alloyed with Bi, Pb, Cu or Pt, rhodium is soluble in HNO_3. It is attacked by Cl_2, forming $RhCl_3$.[3] The oxide, Rh_2O_3, is slightly soluble in excess of concentrated alkali hydroxide. The dioxide, RhO_2, is insoluble in H_2O or alkalis. It dissolves in HCl with evolution of Cl_2. Rhodium trichloride, $RhCl_3$, obtained by chlorination of the metal, is insoluble in H_2O or acids; the hydrated salt is readily soluble. The nitrate and sulfate of Rh^{+3} are readily soluble, the double nitrites — except sodium — $Rh(NO_2)_6^{-3}$, insoluble to slightly soluble.

6. Reactions. — Alkali hydroxides and carbonates slowly precipitate Rh^{+3} as the yellow hydroxide, $Rh(OH)_3$ ($Rh_2O_3 \cdot 3H_2O$). From a hot solution the product is darker, and from a sulfate solution the separation is more rapid than from that of the chloride. The precipitate dissolves in excess of NH_4OH. Potassium nitrite forms an orange-yellow precipitate with Rh^{+3}, soluble in HCl. From a hot solution, H_2S precipitates brown Rh_2S_3, insoluble in the alkali sulfides (distinction from Pt and Ir), soluble in HNO_3. If precipitated in a cold solution, the sulfide is soluble in alkali sulfides. KI precipitates, from hot solution, a dark brown rhodium iodide, RhI_3. Sodium phosphate and borax give precipitates with Rh^{+3}, but oxalic acid and $SnCl_2$ do not. Cyanides[4] form, with Rh^{+3}, the complex ion $Rh(CN)_6^{-3}$. Metallic Zn or Mg precipitates Rh° from solutions of its ions.

7. Ignition. — Fusion of Rh° with NaOH and KNO_3 gives RhO_2. Repeated fusion with $K_2S_2O_7$ forms a sulfate soluble in H_2O (distinction from Ru). The yellow solution turns red on addition of HCl.

8. Detection. — *a.* After separation as indicated above, Rh may be identified: (1) Ferro- and ferricyanides, when heated with Rh^{+3}, give a greenish-brown color. (2) Ag^+, Hg_2^{++} and Pb^{++} produce a rose-red color in Rh^{+3} solutions. (3) Heating a solution of $(NH_4)_2RhCl_6$ with concentrated NH_4OH precipitates the yellow chloride, $RhCl(NH_3)_5Cl_2$, insoluble in 6 *N* HCl. (4) Heated with NaCl in an atmosphere of Cl_2, rhodium forms $Na_3RhCl_6 \cdot nH_2O$, which dissolves in H_2O to form a rose-red solution. (5) If 40% $SnCl_2$ in 30% HCl is added to a mineral acid solution of a rhodium salt and the mixture heated to boiling, a brown color develops that changes to a raspberry color on cooling. The test will detect 0.0_36 mg. Rh in 1 cc.[5]

b. Rh (and Ir) may be precipitated as the sulfide in Group II. After dissolving in aqua regia, acetic acid and $NaNO_2$ are added to the solution. Upon making alkaline with NaOH, all metal ions, except Rh and Ir, precipitate as hydroxides. The $Na_3Rh(NO_2)_6$ and $Na_3Ir(NO_2)_6$ left in solution may be separated as already indicated.

9. Determination. — Rhodium is usually precipitated and weighed as the metal.

10. Oxidation and Reduction. — Solutions of Rh salts are reduced to the metal by Zn or Mg. All Rh compounds are converted to the metal by heating in a current of hydrogen.

[1] Wichers, *J. Am. Ch. Soc.*, **46**, 1818 (1924).

[2] Gutbier, *et al.*, *Z. anorg. allgem. Ch.*, **95**, 225 (1916).

[3] Gutbier, *et al.*, *Ibid.*, **95**, 225–46, 247–52 (1916), *C.A.* **11**, 2307, consider the action of Cl and Br on Rh°. Cf. Wöhler and Müller, *Ibid.*, **149**, 125 (1925); *C.A.* **20**, 344.

[4] Cf. Krauss and Umbach, *Z. anorg. allgem. Ch.*, **179**, 357–68 (1929); *C.A.* **23**, 2673.

[5] Ivanov, *J. Russ. Phys. Ch. Soc.*, **50**, I, 460–2 (1918); *C.A.* **17**, 3306.

§106. Palladium (planet *Pallas*). Pd = 106.7. Atomic No. 46. Valence 2, 4 (1, 3). Discovered by Wollaston in 1803.

1. Physical Properties. — Density, 12.25 ± 0.04;[1] melting point, 1553° ± 2°;[2] boiling point, 2200°. Palladium is a silvery white metal, ductile and malleable, conducting electricity about one-eighth as well as Ag. Palladium softens at temperatures distinctly below the melting point, hence it can be welded easily. When only slightly heated, the metal assumes a rainbow appearance, the colors grading from green to violet. Because of its general properties, Pd is classed with the platinum metals, yet in its reaction with acids it is markedly different. In the air, at room temperatures, it is but slightly tarnished. At a red heat, however, it becomes covered with a coating of the oxide. The molten metal absorbs oxygen and on cooling "spits" like silver. The finely divided metal, palladium sponge, absorbs many times (1000 to 3000) its volume of H_2,[3] forming the hydride; it retains most of the gas even at 100°. Acetylene is also absorbed to the same or even a greater extent. Palladium is used in making non-magnetic watches and parts of delicate balances. Alloyed with gold, e.g., "palau," palladium is used as a substitute for Pt in making crucibles, etc., for chemical work. In dental work palladium is being used less extensively than formerly as "platinum metal."

2. Occurrence. — Palladium is a never-failing element in the platinum ores, native or alloyed with Pt, Au or Ag. It forms 1%–2%[5] of the metal. In 1929 the United States imported slightly over 24,350 ounces of palladium. During that year the average price was $39 per ounce; by the following July it had dropped to $23–$24 per ounce.[6]

3. Preparation. — According to Noyes and Bray,[7] the chloride solution of Pt, Ir, Pd and Rh is treated with HCl, evaporated, the Pt and Ir precipitated with NH_4Cl, and the Pd removed from the filtrate as $(NH_4)_2PdCl_6$ by addition of Cl_2 gas.[8] Ignition yields Pd.

4. Oxides and Hydroxides. — Palladium monoxide, PdO, black, is the most stable of the oxides of Pd. It is formed by prolonged heating of the metal slightly above 700°, by gentle ignition of $Pd(NO_3)_2$, or by the precipitation of brown $Pd(OH)_2$ from $PdCl_2$ with Na_2CO_3. Ignition of the precipitate gives PdO. Palladium dioxide, PdO_2, is obtained from the nitrate by anodic oxidation. When gently ignited (ca. 200°), it loses half of its oxygen, becoming PdO.

5. Solubilities. — *a. Metal.* — Palladium is slowly dissolved by boiling HCl or H_2SO_4; HNO_3 dissolves it, even in the cold, forming $Pd(NO_3)_2$. It is more readily soluble in aqua regia, forming H_2PdCl_4. It is not affected by H_2S. When fused with $K_2S_2O_7$, it becomes $PdSO_4$.

b. Oxides. — PdO is insoluble in H_2O, soluble in acids, forming Pd^{++}, soluble in concentrated NH_4OH. The hydroxide, $Pd(OH)_2$, reacts similarly. Palladium dioxide, PdO_2 is unstable; when freshly prepared, boiling with H_2O will cause decomposition. It is readily soluble in HCl, forming $PdCl_2$ and Cl_2.

c. Salts. — Palladous chloride, bromide and iodide are moderately soluble to insoluble, this property decreasing in the order mentioned. They form complex salts, more or less readily, of the type K_2PdCl_4. The complexes are, in general, more soluble than the simple salts. Palladous nitrate, $Pd(NO_3)_2$, is soluble in dilute HNO_3; dilution, evaporation or standing causes decomposition with precipitation of a basic nitrate. Palladous sulfate, $PdSO_4$, is readily soluble in H_2O but decomposes upon standing. Palladium tetra-

[1] Davey, *Phys. Rev.*, [2] **25**, 753 (1925).

[2] Fairchild, *et al.*, *B. Stds. J. Research*, **2**, 931 (1929); Schofield, *Proc. Roy. Soc.* (London), **A125**, 517–31 (1929); *C.A.* **24**, 279–80, gives 1555° ± 2°.

[3] Paal and Gerum, *Ber.*, **41**, 805 (1908).

[4] Latimer and Hildebrand, p. 327.

[5] Cf. Friend, IX, 1, p. 257.

[6] Mineral Ind., **1929**, p. 502–15.

[7] Noyes and Bray, p. 110.

[8] **For other methods, see: Friend, IX, 1, Chapter X. It is understood that a precious metal refinery is a high grade analytical laboratory on a large scale.**

chloride and tetrabromide have not been prepared in a pure state. The alkali complexes, however, e.g., $CaPdCl_6$, are more stable, and soluble in H_2O and alcohol. The potassium and ammonium salts, K_2PdCl_6 and $(NH_4)_2PdCl_6$, are slightly soluble in H_2O, insoluble in alcohol, and partially decomposed by both solvents.

6. Reactions. — The fixed alkali hydroxides precipitate Pd as a brown, basic salt or as brown palladium hydroxide, soluble in excess of the hot reagent. NH_4OH gives a flesh-red precipitate which is soluble in excess of the ammonia, and from this solution reprecipitated by HCl as yellow palladosammine, $Pd(NH_3)_2Cl_2$. The fixed alkali carbonates precipitate the hydroxide; $(NH_4)_2CO_3$ acts like the hydroxide. Alkaline tartrates or citrates give a yellow precipitate, in neutral solutions of $Pd(NO_3)_2$. Potassium cyanide precipitates palladous cyanide, $Pd(CN)_2$, white, soluble in excess of the reagent to form $Pd(CN)_4^{--}$. Potassium thiocyanate, even in the presence of SO_2, does not give a precipitate (distinction from Cu). Phosphates give a brown precipitate. H_2S or S^{--} precipitates dark brown to black palladous sulfide, PdS, insoluble in $(NH_4)_2S$, soluble in HCl and aqua regia. KI precipitates Pd^{++} as palladous iodide, PdI_2, black, visible in 500,000 parts of the solution. It is insoluble in H_2O, alcohol and ether; soluble in excess of the reagent. At a red heat the compound decomposes SO_2 precipitates Pd° from solutions of the nitrate or sulfate, not from the chloride. If $FeSO_4$ is added to a solution of $Pd(NO_3)_2$, a black precipitate of the metal slowly forms. $SnCl_2$ produces a brown to black precipitate, soluble in HCl to give a green solution. Acetylene passed into an acid solution of Pd^{++} forms a brown precipitate (quantitative separation from Cu). (Caution!! Metal acetylides are in general very explosive.) If CO is passed into a solution of Pd^{++}, the Pd° thus formed reduces MoO_4^{--}, or a phosphomolybdate, to molybdenum-blue. Apparently the reaction is specific for Pd among the platinum metals.[1]

7. Ignition. — Nearly all palladium compounds are reduced by heat to the metal sponge. An asbestos thread will become incandescent if wet with the solution of a Pd salt, ignited, and after cooling, held in a stream of unlighted gas. This is a very delicate test for the platinum metals.[2]

8. Detection. — In the usual scheme of analysis, Pd^{++} is precipitated as the sulfide in Group II and separated along with the Cu division, due to its insolubility in $(NH_4)_2S_x$. Subsequent separations depend upon the other metals present.[3] The identification of Pd[4] is effected by the reactions mentioned in (6), also by the following characterizing tests: (1) α-nitroso-β-naphthol gives a red-brown precipitate when added to a solution of Pd^{++} (distinction from other platinum metals).[5] The test will detect 0.001 mg. of Pd per cc. (2) Diacetyldioxime forms a yellow palladous dioxime, $(C_4H_7N_2O_2)_2Pd$, with Pd^{++} in acid solution[6] (distinction from Ni^{++}). (3) Tincture of alkanet root, treated with a few drops of Pd^{++} solution, changes in color from red to orange yellow, steel gray, and finally green. After standing for some time, the red color returns. These changes have been studied spectroscopically.[7] (4) Benzoylmethylglyoxime[8] appears to be a specific reagent for Pd^{++}. The precipitate formed in acid solution is $C_{20}H_{18}N_4O_6Pd$.[9]

9. Determination. — *Gravimetrically*, Pd may be precipitated as the metal, K_2PdCl_4, dioxime[10] (possibly the best for small amounts), $Pd(CN)_2$,[11] PdI_2,[12] etc., and weighed as the

[1] Feigl and Krumholz, *Ber.*, **63B**, 1917–9 (1930); *C.A.* **25**, 50.

[2] Curtman and Rothberg, *J. Am. Ch. Soc.*, **33**, 718–24 (1911).

[3] For the Noyes and Bray procedure, see (3) above.
Friend, IX, 1, p. 342–5, gives four schemes.

[4] Bredig and Fortner, *Ber.*, **37**, 798 (1904), state that as little as 1 mg. of colloidal Pd in 2600 liters of liquid may be detected by the use of NaOH and H_2O_2.

[5] Schmidt, *Z. anorg. allgem. Ch.*, **80**, 335 (1913).

[6] Wunder and Thüringer, *Z. anal. Ch.*, **52**, 101 (1913).

[7] Formánek, *Z. anal. Ch.*, **39**, 681 (1900).

[8] Hanuš, *et al.*, *Ch. News*, **131**, 401–2 (1925); **132**, 1–4 (1926); *C.A.* **20**, 1368.

[9] Ogburn, *J. Am. Ch. Soc.*, **48**, 2507–12 (1926), has studied the action of some 120 different reagents on the platinum metals.

[10] Davis, U. S. Bur. Mines Rept., No. 2351 (1922); *C.A.* **16**, 2280; cf. Zschiegner, *Ind. Eng. Ch.*, **17**, 294 (1925).

[11, 12] Useful for the separation of large amounts of Pd.

metal after ignition in H_2, or as the dioxime after drying at 105°. Several of the methods mentioned under (8) have been applied quantitatively.[1,2]

10. Oxidation and Reduction. — Pd° is precipitated from solution by H_2SO_3, $SnCl_2$, H_3PO_2, sodium formate, hydrazine sulfate, and all the metals that precipitate Ag (§59, 10). $FeSO_4$ reduces Pd from $Pd(NO_3)_2$ but not from $PdCl_2$. Alcohol at the boiling point reduces Pd^{++}; oxalic acid does not (distinction from Au, §73, 6, *b*).

§107. Iridium (L. *iris* = rainbow). Ir = 193.1. Atomic No. 77. Valence (2), 3, 4 and 6. Discovered by Tennant in 1803.

1. Physical Properties. — Density, 22.4;[3] melting point, 2350° (?);[4] boiling point, 4800°. Iridium, when reduced by H_2 is a gray powder, which, by pressing and igniting at a white heat, changes to a metallic mass capable of taking a polish. In appearance it is similar to silver. It is not ductile. It is used chiefly as an alloy with Pt, forming a very hard, durable material for standard weights, fountain pen points, etc. A Pt-Ir alloy containing 25%–30% Ir is not attacked by aqua regia.

2. Occurrence. — Iridium is found in the platinum ores to the extent of 1%–10% of the crude metal.[5] It also occurs as osmiridium, a native alloy containing 50%–75% Ir. During 1929 the price of Ir fluctuated between $180 and $450 per ounce. The average was $229.[6]

3. Preparation. — Iridium may be obtained by dissolving osmiridium in molten Zn. The product is treated with HCl and the residue thus obtained converted to the chlorides. Osmium is removed as OsO_4 by distillation, leaving Ir and small amounts of other platinum metals in the residue. Suitable purification, after precipitation as ammonium chloroiridate, $(NH_4)_2IrCl_6$, to remove traces of Pt, Ru, etc., will yield a product that can be converted to the metal Ir°.[7]

4. Oxides and Hydroxides. — While other oxides have been reported, the two best established are Ir_2O_3 and IrO_2. The hydrated sesquioxide is obtained in an impure state by adding an alkali to $IrCl_3$ in an inert atmosphere(CO_2), evaporating to dryness, and extracting the residue with NaOH and H_2SO_4 alternately. The dioxide, IrO_2, is obtained by heating Ir° at a bright red heat[8] or igniting Ir_2O_3 above 400°. Iridic hydroxide, $Ir(OH)_4$, is formed by adding an excess of fixed alkali to $IrCl_6^{--}$ and boiling.

5. Solubilities. — Freshly precipitated Ir° may be dissolved in aqua regia. The ignited metal and the compact form are insoluble in all acids. The best solvent is Cl_2. IrO_2 is insoluble in acids. $IrCl_3$ is soluble in H_2O and forms double chlorides, e.g., $(NH_4)_3IrCl_6$, with the alkali chlorides. These salts are soluble in H_2O but insoluble in alcohol. The higher valence salts, e.g., $(NH_4)_2IrCl_6$, are only slightly soluble in H_2O.

6. Reactions. — The fixed alkali hydroxides or carbonates precipitate from boiling solutions of $IrCl_3$ or $IrCl_4$, dark blue $Ir(OH)_4$, insoluble in all acids except HCl. Potassium nitrite, added to hot solutions of iridium salts, gives first a yellow color and finally a yellow precipitate insoluble in H_2O or acids. H_2S reduces Ir^{+4} to Ir^{+3} and then precipitates Ir_2S_3, brown, soluble in alkali sulfides. Sulfurous acid precipitates Ir°, black, from

[1] Cf. Ogburn and Riesmeyer, *J. Am. Ch. Soc.*, **50**, 3018 (1928), for the use of 6-nitroquinoline.

[2] Singleton, *Ind. Chemist*, **3**, 121–4 (1927); *C.A.* **21**, 1606, has described several colorimetric tests. Cf. Rüdisüle, IV; and Hillebrand and Lundell, Chapter XIX.

[3] Mylius and Dietz, *Ber.*, **31**, 3188 (1899).

[4] B. Stds. Cir. 35.

[5] Cf. Friend, IX, 1, p. 257.

[6] Mineral Ind., **1929**, p. 507.

[7] Cf. Noyes and Bray, p. 110.

[8] 800°. Cf. Wöhler and Witzmann, *Z. anorg. allgem. Ch.*, **57**, 323 (1908); *C.A.* **2**, 1794; Krauss and Gerlach, *Z. anorg. allgem. Ch.*, **143**, 125; **147**, 265 (1925); *C.A.* **19**, 1544.

hot solutions. Potassium and ammonium chloride form respectively the dark-colored, slightly soluble K_2IrCl_6 and $(NH_4)_2IrCl_6$. Metallic Zn precipitates Ir° from hot solutions. Formic acid effects the same result.

7. Ignition. — When Ir° is fused with $K_2S_2O_7$ it is oxidized, but the product does not dissolve (distinction from Rh°). Ignition on charcoal reduces all iridium compounds to Ir°. Fusion in the air with NaOH or $NaNO_3$ causes oxidation of the metal, the iridium oxide being partially soluble in the fixed alkali.

8. Detection. — *a.* The double chlorides of Pt, Ir, Pd and Rh are evaporated with NH_4Cl, thus precipitating $(NH_4)_2PtCl_6$ and $(NH_4)_2IrCl_6$. After filtration, the residue is dissolved in aqua regia, evaporated to remove excess acid, diluted and then treated with $NaHCO_3$ and Br_2, whereupon black IrO_2 precipitates.[1] Confirmatory tests may be applied as suggested in (6).

b. If a few drops of a 1% solution of the leuco base of malachite green in concentrated acetic acid are added to 8–10 cc. of a solution containing $IrCl_6^{--}$, the characteristic color of the malachite green will appear at once. The interferences are Cl_2, halides of Au^{+3}, and $PdCl_6^{--}$. The test will detect one part of Ir in six million.[2]

9. Determination. — Iridium may be precipitated as $(NH_4)_2IrCl_6$, ignited in hydrogen, and weighed as the metal.

10. Oxidation and Reduction. — Formic acid (from hot solution), and Zn with H_2SO_4 or HCl reduce Ir compounds to the metal. $SnCl_2$, $FeSO_4$, $H_2C_2O_4$ and NH_2OH reduce Ir^{+4} to Ir^{+3} (separation from Au, §73).

§108. Osmium (Gr. *osme* = odor).[3] Os = 190.8. Atomic No. 76. Valence 2, 3, 4, 6 and 8. Discovered by Tennant in 1803.

1. Physical Properties. — Density, 22.48,[4] the heaviest of all substances; melting point, 2700° (?);[5] boiling point, > 5300°. Osmium, in the compact form, is very hard. Like the diamond it will cut glass. It possesses a metallic luster, and a bluish color resembling Zn°. In the absence of air, Os may be heated above the vaporization point of Pt without oxidation; but exposed to the air at about 425° it burns, forming the odorous, poisonous perosmic oxide, OsO_4.

2. Occurrence. — Osmium occurs native with platinum. The crude metal contains 1%–10% Os. The native alloy, osmiridium, contains 20%–40% Os. In 1929 the price was $55–$65 per ounce.

3. Preparation. — Osmiridium, or other material containing Os, is finely divided, then boiled with aqua regia, whereupon OsO_4 distills over and is absorbed in NaOH, forming $Na_2OsO_5 \cdot H_2O$. Acidification of the distillate and reduction with any of the common metals, Zn, Mg, Hg, etc., causes separation of metallic Os.

4. Oxides and Hydroxides. — Four oxides of Os have been reported, OsO, Os_2O_3, OsO_2 and OsO_4. The first three are basic, the last a somewhat indifferent peroxide. Osmium monoxide, gray, has been prepared by thermal decomposition of the sulfite, $OsSO_3$. A solution of osmium trichloride, $OsCl_3$, when treated with an excess of Na_2CO_3, forms Os_2O_3, black. Hydrolysis of osmium tetrachloride yields OsO_2.[6] The tetroxide,[7] OsO_4, is formed by direct combustion of the metal in air (cf. 1), or by oxidation with hot concentrated HNO_3. It exists as colorless, glistening needles, melting around 40°, moderately soluble in H_2O. Its solutions have a very penetrating odor, resembling that

[1] Noyes and Bray, p. 110.

[2] Chugaev, *Ann. inst. platine*, **7**, 205–7 (1929); *C.A.* **24**, 2689.

[3] From the odor of the tetroxide.

[4] I. C. T.

[5] B. Stds. Cir. 35.

[6] Cf. Ruff and Rathsburg, *Ber.*, **50**, 484 (1917).

[7] Cf. Fritzman, *Ann. inst. platine*, **7**, 138–60 (1929), *C.A.* **24**, 3452; Krauss and Schrader, *Z. anorg. allgem. Ch.*, **176**, 385–97 (1928), *C.A.* **23**, 1073.

of chlorine. The fumes of the acid are very poisonous and cause inflammation of the eyes. (H_2S has been recommended as an antidote.)

5. Solubilities. — *a.* The metal in compact form is not attacked by acids. The precipitated metal, i.e., finely divided, is slowly dissolved by aqua regia or fuming HNO_3.

b. The oxide, OsO_4, dissolves in H_2O to the extent of 5.8 g./100 g. of solution at 15°.

c. The salts of Os^{++} and Os^{+3} do not appear to be stable in aqueous solution; $OsCl_4$ and OsS_2 are slightly soluble, OsS_4 is insoluble in H_2O. The more complex salts, as those of $OsO_2Cl_4^{--}$ and $OsO_3Cl_2^{--}$, are but slightly soluble.

6. Reactions. — The fixed alkali hydroxides, ammonia, and the alkali carbonates precipitate brown osmium hydroxide, $Os(OH)_4$. Potassium nitrite reduces osmic acid to osmous acid, which forms a red salt. H_2S precipitates brown osmium sulfide, OsS_2, in the presence of a mineral acid, and gives OsS_4 in a neutral solution. Both compounds are insoluble in $(NH_4)_2S$. Sodium sulfite (or SO_2) reduces Os^{+8} to Os^{++}. This is accompanied by a change in color of the solution through violet to blue, and finally precipitation of $OsSO_3$. Ferrous sulfate produces a black — $SnCl_2$ a brown — precipitate, soluble in HCl.

7. Ignition. — Osmium when heated on a piece of Pt foil, gives an intensely luminous flame of short duration. By holding the foil in the reducing flame and then again in the oxidizing zone, the luminescence may be repeated. If a mixture of the metal or the sulfide and KCl is heated in Cl_2 gas, there is formed a double salt of potassium osmic chloride, slightly soluble in cold H_2O, more readily in hot H_2O. Alcohol precipitates the salt as a crystalline, red powder.

8. Detection. — *a.* Osmium is detected by the intensely luminous flame when ignited on Pt foil (7); by oxidation and distillation (as OsO_4) into NaOH with production of a yellow to orange color; by the odor of OsO_4; and by the black precipitate formed with H_2S.

b. An intense red color is produced when sodium chloro-osmate is boiled with thiourea in the presence of a little HCl. The test will detect one part of Os in 100,000 of solution.[1] Traces of Os may be detected by the distinct blue color obtained when KCNS is added to an acid solution of OsO_4. Extraction with ether gives a delicacy of one part in a million of solution.[2]

9. Determination. — Osmium may be separated as the tetroxide, by distillation, converted to the metal, and weighed.

10. Oxidation and Reduction. — OsO_4 is reduced to OsO_2 by $FeSO_4$. Zn and many other metals, in the presence of strong acids, precipitate Os^0. The same product is obtained by ignition of all osmium compounds in H_2 (cf. 6).[3]

§109. Tungsten (Swedish, *tung sten* = heavy stone). Wolframium; W = 184.0. Atomic No. 74. Valence 2 to 6. Discovered by d'Elhujar in 1783–6. (Scheele isolated the oxide in 1781.)

1. Physical Properties. — Density, 19.32 ± 0.02;[4] melting point, 3382°.[5] Tungsten is a silver white to steel gray, brittle metal. Its hardness is 6.5 to 7.5. It is non-magnetic, stable in air at ordinary temperatures, acquires temper colors on heating, burns at a high temperature, and decomposes steam at a red heat. Its chief uses are: as an electric light filament, and to make alloy steel, 16%–20% W being generally employed for a very tough tool steel that will hold its edge at a red heat. More recently, an alloy of tungsten carbide and cobalt (variously known as "carboloy," "widia," "hart metal," etc.), has been advocated for cutting tools. This material will readily cut glass and out-

[1] Chugaev, *Z. anorg. allgem. Ch.*, **148**, 65 (1925). Cf. *Compt. rend.*, **167**, 235 (1918).

[2] Hirsch, *Ch. Ztg.*, **46**, 390 (1922); *C.A.* **16**, 2279.

[3] Cf. Ruff and Bornemann, *Z. anorg. allgem. Ch.*, **65**, 429–56 (1910), *C.A.* **4**, 1721; Paal and Amberger, *Ber.*, **40**, 1378–91 (1907), *C.A.* **1**, 1521.

[4] Davey, *Phys. Rev.*, **26**, 736–8 (1925), (X-ray).

[5] Forsythe and Worthing, *Astrophys. J.*, **61**, 146–85 (1925).

wear the usual high-speed cutting tools.[1] Haynes' "stellite" is another very hard tungsten alloy, consisting essentially of Co, 55%; Cr, 35%–40%; W, 3%–10%.

2. Occurrence. — Tungsten does not occur in nature in large amounts, nor is it widely disseminated. The most common minerals are scheelite, $CaWO_4$, and wolframite $(FeMn)WO_4$.[2] Due to low labor costs, China dominates the field of production. From her deposits of wolframite, in 1928, 6600 metric tons of 60% WO_3 were produced. The United States[3] produced about 1200 tons, and Burma the same amount. The total production for the year mentioned was 14,000 tons, valued at slightly over $600 per ton. The powdered metal is quoted at about $1.60 per pound.

3. Preparation. — (1) Reduction of WO_3 (cf. 4)[4] with carbon[5] or hydrogen.[6] (2) Reduction of tungsten chloride alone[7] or by use of hydrogen and carbon. While reduction of WO_3 with carbon is perhaps somewhat cheaper, the use of hydrogen gives a more easily controlled process. Carefully purified WO_3 is heated slowly (2–3 hours) to about 700°, in an atmosphere of pure dry hydrogen.[8] The brown WO_2 thus obtained may or may not be mixed with more WO_3 before further heating. Subsequent reduction at 780–1100° (the higher the temperature, the coarser the resulting powder), gives pure metallic tungsten, which by "swaging" may be formed into a ductile wire.

4. Oxides. — Tungstic oxide, WO_3,[9] lemon yellow, is obtained by fusing the ore, e.g., wolframite, with Na_2CO_3 (and $NaNO_3$). The Na_2WO_4 thus formed is extracted with H_2O and the solution acidified, whereupon the WO_3[10] precipitates. Solution of the product in ammonia and subsequent precipitation with acid, followed by calcination, yields a fairly pure oxide. The density of amorphous WO_3 is 7.16 at 17°.[11] It is more magnetic than the metal, does not decompose upon heating to 1750°, but may be readily reduced to lower oxides or the metal by hydrogen, carbon, etc. The greenish tinge often noted may be due to a slight surface reduction, at room temperature, by traces of organic matter.[12] The characteristic yellow color is restored by heating in air. Tungstic oxide is converted by chlorine to $WOCl_2$ and by H_2S to WS_3. Many types of tungstates have been reported in the literature. Among these, two have been well established, i.e., normal tungstates of the formula $R_2WO_4 \cdot nH_2O$, and paratungstates, in which $R_2O : WO_3 = 3 : 5$ or $5 : 12$. The metatungstates, $R_2W_4O_{13} \cdot nH_2O$, are also fairly well established. Recently another series has been reported.[13] It is said to be of the type: $4R_2O \cdot 10WO_3 \cdot nH_2O$. Tungsten dioxide, WO_2, brown, is obtained upon reduction of WO_3 with hydrogen below 700°. It is stable in air, readily oxidized by oxides of nitrogen and chlorine; Hg^{++} and Cu^{++} are reduced to Hg_2^{++} and Cu_2^{++}; $(NH_3)_2Ag^+$ forms Ag°; concentrated NaOH dissolves the amorphous form with liberation of hydrogen and formation of a tungstate; reduction to the metal is readily effected by heating in hydrogen or with carbon above 700°. Ditungsten pentoxide, W_2O_5,[14] blue, may be obtained by reduc-

[1] Hoyt, *Gen. Electric Rev.*, **31**, 585–91, (1928), *C.A.* **23**, 42.

[2] The average composition is FeO = 10%, MnO = 14%, WO_3 = 75%. Ores high in Mn are called hübnerite.

[3] California has been credited with the purest scheelite deposits in the world. Colorado excels in ferberite (iron tungstate). Nevada and Washington both have deposits of scheelite. (Mineral Ind., **1928**, p. 607 *et seq.*).

[4] For methods of preparing WO_3 from ores and details of metallurgy, see: Smithells, "Tungsten," London, Chapman and Hall, **1926**, p. 9–54.

[5] Davis, *Ind. Eng. Ch.*, **11**, 201 (1919).

[6] Ruff, *Z. angew. Ch.*, **25**, 1889 (1912); Davis, *loc. cit.*

[7] Pring and Fielding, *J. Ch. Soc.*, **95**, 1502 (1909).

[8] von Liempt, *Z. anorg. allgem. Ch.*, **120**, 267 (1922), gives diagrams showing equilibrium conditions between the oxides, metal, hydrogen and water vapor.

[9] Commercially called tungstic acid because of its acidic properties.

[10] If precipitation is effected from a hot solution with concentrated acid, yellow $WO_3 \cdot H_2O$ is obtained; from a cold solution, white $WO_3 \cdot nH_2O$ separates.

[11] Smith and Exner, *Ch. News*, **90**, 66 (1904).

[12] von Liempt, *Z. anorg. allgem. Ch.*, **119**, 310 (1921).

[13] *Smith, J. Am. Ch. Soc.*, **44**, 2027 (1922).

[14] $(WO_2)_2WO_4$ has been suggested as the probable formula.

ing WO_3 with hydrogen at 250–300° or by boiling WO_3 with Sn and HCl.[1] This intermediate oxide is unstable and, since difficult to isolate, little is definitely known about its properties. Several other oxides of tungsten have been reported (W_4O_3, W_2O_3, W_5O_{14}, etc.), but the composition of none of them has been clearly established.

5. Solubilities. — *a. Metal.* — Tungsten is only slightly attacked by HCl or H_2SO_4, slowly by HNO_3 or aqua regia; slowly soluble in the alkalis. The best solvent is a mixture of concentrated HNO_3 and HF.[2]

b. Oxides. — The amorphous dioxide, WO_2, is readily soluble in warm HCl and H_2SO_4 to give a red colored solution, which, upon standing, loses its color due to oxidation of the tungsten. The amorphous dioxide is also soluble in alkali hydroxides to form tungstates with the evolution of H_2. The crystalline dioxide is not affected by hot concentrated acids or alkalis. Tungstic oxide, WO_3, is insoluble in H_2O and most acids, even hot concentrated H_2SO_4; soluble in HF,[3] NaOH, Na_2CO_3 and NH_4OH. $WO_3 \cdot H_2O$ is insoluble in H_2O. It reacts with bases to form normal, di-, tri- and para-tungstates. In an atmosphere of CO_2, it reacts with the chlorides of Ca, Mg, Co, Ni and Fe (not with those of Pb, Ag, K and Na): $MCl_2 + 2\,WO_3 = MWO_4 + WO_2Cl_2$. Heated with chlorine, WO_2Cl_2 is formed (also some WCl_4). It is decomposed by H_2O. Sulfur, H_2S, or HgS forms WS_3 on heating with WO_3. Soluble alkali tungstates are formed by fusion of WO_3 with the alkali carbonates; more slowly by boiling with the carbonates. Acids form, from solutions of the alkali tungstates, a white precipitate of $WO_3 \cdot nH_2O$, turning yellow on boiling; insoluble in excess of the acid (distinction from MoO_3); soluble in NH_4OH. Phosphoric acid changes tungstic acid to metatungstic acid, $H_2W_4O_{13}$, or phosphotungstic acid, $P_2O_5 \cdot 12WO_3 \cdot nH_2O$, which is soluble in H_2O and not precipitated by other acids. Long boiling of the solution of metatungstic acid causes the precipitation of WO_3. Fusion of WO_3 with $K_2S_2O_7$ gives a complex of potassium tungstate and WO_3, not readily soluble in H_2O but very easily soluble in $(NH_4)_2CO_3$ (distinction from SiO_2).

c. Salts. — The halide salts; e.g., WCl_4, WCl_5, WCl_6, WO_2Cl_2, $WOCl_4$, are all more or less rapidly decomposed by H_2O. WS_2 is insoluble in H_2O and in most acids; aqua regia has slight effect, but a mixture of HNO_3 and HF dissolves it readily. It is readily decomposed by molten alkalis. WS_3 is slightly soluble in H_2O, easily soluble in alkaline hydroxides, carbonates and sulfides. Normal tungstates of the alkalis[4] and Mg are soluble in H_2O, those of the other metals, slightly soluble to insoluble, not only in H_2O but also in dilute acids. Concentrated mineral acids (not H_3PO_4) decompose them, giving WO_3. Paratungstates gradually decompose in H_2O to form normal and metatungstates. Commercial sodium tungstate is generally the para salt,[5] the solubility of which, at 22°, is about 8 g./100 g. of H_2O. Metatungstic acid is readily soluble in H_2O (at 22°–75.65 g./100 g. of H_2O[6]); a dilute solution is quite stable when cold; $WO_3 \cdot 2H_2O$ gradually precipitates from concentrated solutions. Metatungstates, $R_2W_4O_{13} \cdot nH_2O$, with the exception of Pb^{++} and Hg_2^{++} salts, are soluble in H_2O, for example, at 15°, one part of ammonium metatungstate is soluble in 0.84 parts H_2O. $BaW_4O_{13} \cdot 9H_2O$ is decomposed by H_2O. Phosphotungstic acid ($P_2O_5 \cdot 12WO_3 \cdot nH_2O$) is very soluble in water; the ammonium and potassium salts are almost insoluble, while the sodium salt is readily soluble.

6. Reactions. — Compounds of tungsten in which this element forms the positive ion, e.g., WBr_4, WI_4, $WOCl_4$, etc., are analytically of comparatively minor importance.

a. The alkali hydroxides form soluble tungstates. Metatungstates react with NH_4OH to form normal tungstates:

$$Na_2W_4O_{13} + 6\,NH_4OH = Na_2WO_4 + 3\,(NH_4)_2WO_4 + 3\,H_2O$$ [7]

[1] The resulting blue solution is said to contain colloidal W_2O_5.

[2] Ruder, *J. Am. Ch. Soc.*, **34**, 387 (1912).

[3] At 50°, 40% HF dissolves 53.7 g. WO_3/100 g. solution, 38% HCl dissolves 0.36 g. WO_3/100 g. solution.

[4] The solubility of $Na_2WO_4 \cdot 2H_2O$ in H_2O at 21° is 42.27 g./100 g. of solution.

[5] Latimer and Hildebrand (p. 287) give $Na_{10}W_{12}O_{41} \cdot 28H_2O$ as the formula.

[6] Friend, VII, 3, p. 236.

[7] Leiser, "Wolfram," Wm. Knapp, Halle, **1910**, p. 87.

b. Oxalic and other organic acids (citric, tartaric), do not precipitate WO_3 from tungstate solutions. If to an alkali tungstate a slight excess of H^+ is added, followed by $K_4Fe(CN)_6$, the solution will become deep reddish brown. Upon standing, a precipitate of the same color is obtained. Thiocyanate and metallic zinc, added to a concentrated HCl solution of a tungstate, give a deep green color. If the CNS^- is added to the WO_4^{--}, then HCl, and finally Zn, a beautiful amethyst color results.

c. If an excess of HNO_3 is added to a cold solution of WO_4^{--}, white $WO_3 \cdot 2H_2O$ will precipitate; boiling changes the solid to yellow $WO_3 \cdot H_2O$. The same reactions are obtained with other mineral acids (except H_3PO_4). Sodium paratungstate heated with H_2O_2 gives sodium peroxytungstate, $NaWO_4 \cdot H_2O$.

d. Sodium hypophosphite added to a tungstate solution containing excess H_2SO_4, gives, upon heating, the blue pentavalent tungsten. Phosphoric acid readily forms complex phosphotungstic acid, which yields no precipitate when treated with mineral acids.

e. Hydrosulfic acid does not precipitate tungsten sulfide from acid or alkaline solution. In the latter, a thio compound, WS_4^{--}, is formed, which decomposes upon acidification to give WS_3. Precipitation, however, is incomplete. If WO_4^{--} is heated with $Na_2S_2O_3$ no action is noted. Upon addition of HCl, a white precipitate and a blue liquid result, the latter being due to a reduction product of the WO_4^{--}. Nitric acid in place of HCl gives a brown liquid.[1] Metatungstic acid is reduced by $(NH_4)_2S$, with formation of the characteristic color. Phosphotungstates are not precipitated by H_2S.

h. Ferrous sulfate, added to WO_4^{--} gives a brown precipitate [of WO_2 (?)]. Upon addition of an acid, no blue color is obtained (distinction from MoO_4^{--}). Stannous chloride added to WO_4^{--} gives a yellow precipitate which becomes blue [$(WO_2)_2WO_4$] upon warming with HCl or H_2SO_4. This is a very delicate test if no interfering substance is present. Metallic Sn or Zn plus acid, gives a blue color with WO_4^{--}. Acetic acid does not interfere with the test when Zn is used, but a brown precipitate is obtained with $SnCl_2$.

j. If a normal or paratungstate solution is treated with Ba^{++}, Ca^{++}, Ag^+ or Pb^{++}, a white precipitate is obtained; mercurous mercury gives a yellow compound. With a metatungstate, Ba^{++} gives no precipitate; $Pb(C_2H_3O_2)_2$ and Ag^+ form complexes.

7. Ignition. — With $NaPO_3$, WO_3 dissolves, on fusion, to a colorless or yellowish bead in the oxidizing flame; in the reducing flame it has a blue color, changing to red on addition of $FeSO_4$. Heated on charcoal in the presence of Na_2CO_3, with a reducing flame the metal is obtained.

8. Detection.[2] — Probably the best test for tungsten involves the reduction to blue $(WO_2)_2WO_4$ in HCl solution by Al°, Zn°,[3] Sn^{++} or $Hg_2(NO_3)_2$ + KI: $3\,H_2WO_4 + SnCl_2 + 2\,HCl = (WO_2)_2WO_4 + SnCl_4 + 4\,H_2O$. The blue quinquivalent tungsten may remain in solution or precipitate, depending on conditions, e.g., in case a soluble complex salt is tested, only a blue solution will be obtained. In addition, reduction may proceed to the formation of a brown color if metals are used.[4] If to a solution of WO_4^{--}, an excess of concentrated HCl is added until any precipitate first formed dissolves, the resulting solution, upon successive additions of small pieces of Zn will develop various colors, especially a brilliant red. Tungstic oxide, treated with 4–5 times its weight of $KHSO_4$ and a few drops of H_2SO_4, is heated to complete solution. More H_2SO_4 is added if necessary to prevent the reprecipitation of the WO_3 on cooling. A drop of this solution treated with (a) phenol, gives a red color, (b) hydroquinone, gives a violet color. The test is more delicate than that using Zn + HCl, since 0.04 to 0.05 mg. is said to be easily detected, whereas with the latter test, 1 mg. is about the lower limit. Pure WO_3 will give a characteristic blue color when rubbed on a bright surface of Fe°, Al°, Zn°, or Cu°; the test is facilitated by slight moistening. The best way is to put WO_3 on Al°, moisten with H_2O, then add 1–2 drops of HCl.[5]

[1] Faktor, *Z. anal. Ch.*, **43**, 410 (1904).
[2] Cf. *h* above.
[3] H_2F_2 interferes.
[4] For detection with Sn: Hartman, *Ch. News*, **114**, 27, 45 (1916).
For detection with Al: Torossian, *Am. J. Sci.*, [4] **38**, 537 (1914).
For detection with $SnCl_2$: Mdivani, *Bull. soc. ch.*, [4] **9**, 122 (1911).
[5] Torossian, *loc. cit.*

Rhodamine B is an excellent reagent for Sb and W. A violet color is obtained if WS_3 is treated with HCl, evaporated to a small volume, sodium nitrate and the reagent added. As little as 0.0_35 mg. of W may be detected.[1]

9. Determination. — *a.* Tungsten may be separated by digesting the solution with HCl or HNO_3, followed by treating with cinchonine to remove the small amount remaining. The precipitate is ignited[2] and weighed as WO_3.

b. Precipitation of tungsten as yellow mercurous tungstate, Hg_2WO_4, followed by ignition to WO_3, is a very satisfactory method in the absence of CrO_4^{--}, MoO_4^{--} and VO_3^-. No satisfactory volumetric methods are available for tungsten, due to the difficulty of obtaining quantitative oxidation (or reduction) from one valence to another.

10. Oxidation and Reduction. — While compounds have been prepared in which the valence of tungsten is 2, 3, 4, 5, or 6, the last is the form usually encountered. This may be reduced to W^{+5} by $SnCl_2$, H_3PO_2, H_2SO_3, etc., in acid solution. The use of metals, as Zn°, Al° (also Fe^{++}), etc., generally gives a lower valence. Reduction to WO_2 takes place by heating in hydrogen below 700°; above 780° the metal is obtained. Peroxides oxidize WO_4^{--} to peroxytungstate, WO_4^-. Heating powdered W° with PbO_2 or $KClO_3$ gives oxidation with incandescence. " Tungsten bronzes " are obtained by reduction of the alkali or alkaline earth tungstates. They are brilliantly colored, insoluble in H_2O and strong acids. Their exact composition is unknown. They are supposed to contain some W^{+4} and W^{+6}.

§110. Rhenium.[3] (*Rhine*, a German province). Re = 186.31 ± 0.02. Atomic No. 75. Valence 4, 6, 7 (and 8). Discovered by Noddack, Tacke and Berg in 1924. Masurium[4] (*Masurian*, a German province). Ma = 98–99. Atomic No. 43. Valence . . . Discovered by Noddack, Tacke and Berg in 1924.

While preparing his periodic table, Mendeléeff found no elements to occupy positions 43 and 75. He therefore prophesied the existence of these elements, named them eka- and dvi-manganese (because of their relationship to Mn), and described some of their properties. Entire confirmation of Mendeléeff's prediction has not been attained, although 60 years have elapsed. Lines corresponding to those of element 43 (eka-manganese) have been found in the X-ray spectrum of certain rare minerals as columbite, sperrylite, etc., but experimentally determined properties have not been reported. Rhenium (dvi-manganese) is somewhat better known.

Originally discovered spectroscopically in tantalite, wolframite and Norwegian columbite, rhenium has been found present in 100 of the 1600 minerals examined by Ida and Walter Noddack.[5] The maximum concentration in any sample was about 0.001% Re.

Commercially,[6] rhenium has been obtained from molybdenite by dissolving large samples in HNO_3, precipitating the Mo as the phosphomolybdate and removing the Re from the filtrate by means of H_2S. The sulfide precipitate, repeatedly subjected to the same series of operations, finally gave a product containing 1% Re. This was oxidized and the Re_2O_7 separated by sublimation. Reduction in hydrogen gave metallic Re as a heavy

[1] Eegriwe, *Z. anal. Ch.*, **70**, 400 (1927).

[2] WO_3 is distinctly volatile above 700°.

[3] Cf. Bur. Mines I. C. 6475.

[4] *Ibid.*

[5] Noddack and Noddack, *Metallbörse*, **20**, 621–2 (1930), *C.A.* **24**, 3959. (Ida Noddack née Tacke). Cf. *Z. physik. Ch.*, **A154**, 207–44 (1931), *C.A.* **25**, 3280.

[6] Cf. Feit, *Z. angew. Ch.*, **43**, 459–62 (1930); Heyne and Moers, *Z. anorg. allgem. Ch.*, **196**, 143 (1931). Using a current density of 0.025 amp./cm.^{2} rhenium may be deposited electrolytically from a neutral or acid solution of an alkali perrhenate.

gray powder having a melting point slightly above 3100°.[1] The density of the powder was about 10.[2]

Metallic rhenium resembles platinum in appearance, is stable in air[3] and, excepting possibly tungsten, is the least fusible of all metals. Its boiling point may be above that of tungsten or carbon. In spite of its rarity, rhenium has recently been made commercially available in the form of the pure metal or as $KReO_4$ at about $4.00 per gram of Re°.[4] The high melting point, temperature of vaporization and hardness of rhenium offer interesting commercial possibilities but thus far the metal has not been used industrially.

Rhenium dioxide, ReO_2, black, is obtained by reduction of ReO_4^-: (1) in concentrated HCl solution with KI, the oxide being precipitated upon addition of a slight excess of NaOH; (2) in 50% KOH solution by solid hydrazine hydrochloride. Rhenium trioxide, ReO_3, red, and intermediate oxides, e.g., Re_3O_8, violet to blue in color, have been mentioned, but their constitution appears to be more uncertain than that of ReO_2.[5] Rhenium heptoxide, Re_2O_7, is readily obtained upon heating Re° in air or oxygen above 150°. It forms yellow, hexagonal crystals that melt at 220° and sublime at a somewhat lower temperature. The white oxide, Re_2O_8, is formed when Re° or a lower oxide is heated in oxygen below 150°. It melts at that temperature and rapidly changes to the heptoxide. The higher oxides of rhenium are acid forming, while the lower oxides are weakly basic.

Metallic rhenium readily dissolves in HNO_3: $3\ Re + 7\ HNO_3 = 3\ HReO_4 + 7\ NO + 2\ H_2O$. It is slowly soluble in H_2SO_4, practically insoluble in HF and HCl. The higher oxides are readily soluble in water, Re_2O_7 forms $HReO_4$, a strong acid that will dissolve hydroxides such as $Al(OH)_3$ and $Fe(OH)_3$ and react with Zn° or Fe° to give H_2. Solutions of the rhenates, ReO_4^{--}, are stable in alkaline media, while the perrhenate ion, ReO_4^-, is stable in acid systems. An aqueous solution of Re_2O_8 reacts like a peroxide. The salts of perrhenic acid are colorless, soluble in H_2O and more stable than the permanganates. The salts of rhenic acid, however, are unstable in solution: $3\ K_2ReO_4 + 2\ H_2O = 2\ KReO_4 + ReO_2 + 4\ KOH$. The solubility of some of the perrhenates is given in Table 36.

Salts of Re^+, Re^{++}, Re^{+3} and Re^{+5} have not been reported as yet. Re^{+4} is more stable and may be obtained by careful reduction of ReO_4^-. The chloride, $ReCl_4$, gives a black

TABLE 36

SOLUBILITY OF SOME PERRHENATES

Compounds	Solubility in g./l. at *ca.* 20°	
$AgReO_4$	3.2	
$NaReO_4$	250.0	
$KReO_4$	12.1	(10.7)*
$CsReO_4$	7.8	
$RbReO_4$	10.2	
$TlReO_4$	1.7	

* Cf. Puschin and Kovač, *Z. anorg. allgem. Ch.*, **199**, 369–73 (1931).

[1] Noddack, *Ibid.*, **21**, 651–2 (1931), *C.A.* **25**, 2930; Agte, *et al.*, *Z. anorg. allgem. Ch.*, **196**, 129–59 (1931), gives 3167° ± 60°.

[2] Goldschmidt, *Naturwissenschaften*, **17**, 134–5 (1929), *C.A.* **23**, 2335, has calculated that the density of pure, massive Re is 21.33. Experimentally, he obtained a slightly higher result. Agte, *et al.*, *loc. cit.*, have reported a density of 20.53.

[3] Oxidation in air commences at about 1000°. If the oxygen content is reduced to 10%, the temperature of initial attack is 1600°. Nitrogen reacts with Re° at about 2500°.

[4] It has been stated [*Chimie & industrie*, **24**, 492 (1930)] that if there is sufficient demand, $KReO_4$ can now be produced at the rate of 400 g. a day to sell for less than the price mentioned above. In 1930 about 300 lb. were made. Cf. Feit, *Z. angew. Ch.*, **43**, 459–62 (1930).

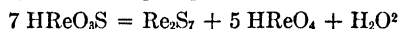
[5] Noddack and Noddack, *Naturwissenschaften*, **17**, 93–4 (1929), *C.A.* **23**, 1833.

precipitate of the hydrated oxide, $ReO_2 \cdot H_2O$, when treated with NaOH or NH_4OH. KCN forms a yellow solution, $K_4Fe(CN)_6$ a blood-red solution. HNO_3 or H_2O_2 readily oxidizes Re^{+4} to Re^{+7}. Salts of Re^{+6} are unstable, those of Re^{+7}, i.e., the perrhenates, $MReO_4$, are very stable. Dilute solutions of ReO_4^- give, with thiocyanates, a yellow color; concentrated perrhenates give, in the cold, a dark red solution that turns black when heated. The addition of Ag^+, Hg_2^{++}, K^+, NH_4^+, Cs^+, Rb^+, or Tl^+ to a solution of ReO_4^-, not too dilute, gives a precipitate of the corresponding salt.

Treatment of ReO_4^- in acid solution, with H_2S gives first a yellow color, then a black precipitate, the rate of separation increasing with the concentration of ReO_4^- and acidity of the system. The precipitate is not appreciably soluble in the alkalis, alkaline sulfides or strong acids. Nitric acid or H_2O_2 oxidizes it to ReO_4^-. As yet the identity of the black compound has not been fully established.[1] When a neutral solution of ReO_4^- is treated with H_2S, a monosulfoperrhenate, ReO_3S^-, is first formed, which soon commences to decompose:

$$4\ KReO_3S = KReS_4 + 3\ KReO_4$$

If the system is acidified, a sulfide is precipitated:

$$7\ HReO_3S = Re_2S_7 + 5\ HReO_4 + H_2O$$ [2]

An alkaline perrhenate treated with H_2S, gives first a pink solution, then a slow deposition of Re_2S_7.[3] If, however, $(NH_4)_2S_x$ is added there is no visible action. Acidification produces a rose-red color, then a gray precipitate slowly forms. In none of the above cases is the precipitation of rhenium as the sulfide quantitative. A complete separation may be effected by adding an excess of $Na_2S_2O_3$ and boiling the acidified solution, whereupon Re_2S_7 separates as a black, amorphous powder.

Metallic rhenium is stable in air below 1000°; fused with NaOH it forms a yellow melt, from which Na_2ReO_4 may be obtained. Alkali perrhenates can be melted without decomposition. Rhenium colors the Bunsen flame pale green, the color appearing and vanishing very soon after coming in contact with the flame.[4] Heated in an ignition tube, rhenium and its compounds give a characteristic sublimate consisting of different colored bands.[5] Neither borax nor phosphate beads give characteristic colors with rhenium compounds.[6] Reduction with Na_2CO_3 on a piece of charcoal gives Re°. Possibly the most delicate test for Re involves an examination of the spark spectrum for lines at 346.5mμ, 346.1mμ and 345.2mμ. If these lines are absent, the amount of Re in the sample is less than 0.001%.[7]

Analytically, rhenium belongs to the hydrogen sulfide group, being precipitated as black Re_2S_7 (see above) from an acid solution of a perrhenate.[8] The precipitate is but slightly soluble in the alkali sulfides. A fairly rapid method for the detection of rhenium -- 0.5% or more -- in the absence of Cr, Mn, Ru and Os, is to fuse a sample with NaOH, whereupon the melt becomes yellow. Further proof may be obtained by extracting the cake with water and adding a slight excess of NH_4OH. Filtration gives a solution of ReO_4^- free from most of the common metals. This may be evaporated to precipitate NH_4ReO_4 or the Re may be removed as the potassium salt, which is less soluble.

A slightly more general method and one that may be used for smaller amounts of Re involves first fusion with NaOH and $NaNO_3$. The melt thus formed is digested in H_2O, any insoluble residue removed and the filtrate acidified with H_2SO_4. Boiling destroys any nitrite present and saturation with H_2S gives, after some time, a precipitate of Re_2S_7

[1] Noddack and Noddack, *Z. angew. Ch.*, **44**, 215–20 (1931), state that the formula is $Re_2S_7 \cdot H_2O$. In *Ber.*, **63**, 16 (1931) they give ReS_3, while in some of their earlier work ReS_2 is mentioned. See also the other reactions mentioned in the text above.

[2] Feit, *Z. anorg. allgem. Ch.*, **199**, 262–70 (1931); *Z. angew. Ch.*, **44**, 65 (1931).

[3] Briscoe, *et al.*, *J. Ch. Soc.*, **1931**, 1439–43.

[4] Agte, *et al.*, *Z. anorg. allgem. Ch.*, **196**, 129–59 (1931).

[5] Geilmann and Wrigge, *Z. anorg. allgem. Ch.*, **199**, 65–76 (1931), state that the test will detect 0.05% Re in a 10 mg. sample.

[6] *Ibid.*

[7] Noddack and Noddack, *Z. angew. Ch.*, **44**, 215–20 (1931).

[8] Noddack, *Metallbörse*, **21**, 651–2 (1931).

contaminated with any V, Mo, W, Ru, Os, Ge, Se, Te and As present. (Should no precipitate separate, it is best to add Na_2MoO_4, which will form MoS_3 and adsorb the Re, thus effecting a concentration.) The sulfide is reduced by heating in hydrogen to 800°. This also removes the last four elements mentioned above. Osmium may be separated as OsO_4 by distillation of the residue dissolved in HNO_3. Re-ignition in H_2, followed by heating (at or above 150°) in O_2, will give a sublimate of Re_2O_7 or Re_2O_8, free from the other elements. The sublimate may be dissolved in H_2O and the ReO_4^- identified by precipitation as $HgReO_4$, $TlReO_4$ or $AgReO_4$. Reduction with a strong reducing agent, e.g., hydrazine hydrochloride, gives a black color. Nitron[1] forms a very insoluble perrhenate, as do also brucin and veratrin.[2] Some reagents that have been suggested for distinguishing Re from Mo are: (1) KCNS, which gives a yellow-red color with dilute solutions of ReO_4^-; concentrated solutions give a dark red color, turning black when heated; (2) ammonium phosphate and potassium ferrocyanide have no effect on ReO_4^-; (3) subjected to sublimation, Re volatilizes first.

Several methods have been suggested for the determination of rhenium. In general they involve precipitation as Re_2S_7, reduction to Re° in a stream of H_2, and finally separation from any impurities still present by fractional sublimation. The Re_2O_7 thus obtained is dissolved in H_2O and the ReO_4^- precipitated, dried and weighed as $KReO_4$,[3] $AgReO_4$,[4] $TlReO_4$[5] or nitron perrhenate.[6] Rhenium may be separated from Mo (except traces) by distillation with HCl from an H_2SO_4 solution.[7] These two elements may also be separated and determined by precipitating the Mo with 8-hydroxyquinoline, from an acetic acid solution, as $MoO_2(C_9H_6ON)_2$. The ReO_4^- is unaffected and may be removed from the filtrate as nitron perrhenate.[8]

Strong reduction of any oxygen compound of Re gives black ReO_2. This in turn is easily reduced to the metal in absence of H_2O. In acid solution Re^{+4} quickly oxidizes to Re^{+7}, but is comparatively stable in an alkaline medium. Dry Re_2O_7 is reduced by H_2 at 300° to ReO_2, at 800° to Re°; CO or SO_2 produces lower oxides and H_2S forms ReS_2. Aqueous solutions of ReO_4^- are easily reduced by Zn°, H_3PO_2 or SO_2, with formation of a yellow color, attributed by some workers to ReO_3. Upon standing, the yellow color disappears. If the rhenium solution is concentrated, a black precipitate is obtained with the Zn°. Alkaline ReO_4^-, with hydrazine, gives a precipitate of ReO_2 (possibly some Re° too). The reaction is rapid if the solution is hot and concentrated. A strongly acid solution of ReO_4^- treated with KI, also gives ReO_2. Evaporation of ReO_4^- with formic acid causes the appearance of a blue color. $SnCl_2$, H_2SO_3 or CH_2O do not reduce ReO_4^- to Re°.

§111. Germanium (L. *Germania* = Germany). Ge = 72.60. Atomic No. 32. Valence 2 and 4. Discovered by Winkler in 1886.

1. Physical Properties. — Density, 5.35;[9] melting point, 958.5°;[10] changes to GeO_2 at 1250°. Germanium is a metallic element belonging to Group IV of the Periodic System. It resembles silicon in brittleness, high melting point, and inertness toward acids and bases. On the other hand it is, like tin, silvery in appearance and has a brilliant luster. In powdered form it is a dull gray. It is very brittle and has a hardness of 6.25 (Mohs'

[1] Geilmann and Voigt, *Z. anorg. allgem. Ch.*, **193**, 311 (1930).
[2] Agte, *et al.*, *Ibid.*, **196**, 129–59 (1931).
[3] Tollert, *Naturwissenschaften*, **18**, 849 (1930).
[4] Noddack and Noddack, *Z. angew. Ch.*, **44**, 215–20 (1931).
[5] Krauss and Steinfeld, *Z. anorg. allgem. Ch.*, **193**, 385 (1929); **197**, 52 (1931).
[6] Geilmann and Voigt, *Ibid.*, **193**, 311 (1930); **195**, 289 (1931).
[7] Geilmann and Weibke, *Ibid.*, **199**, 120–8 (1931).
[8] *Ibid.*, pp. 347–52; cf. Balanescu, *Ann. ch. anal. ch. appl.*, [2] **12**, 259 (1930).
[9] Dennis, *et al.*, *J. Am. Ch. Soc.*, **45**, 2040 (1923).
[10] Dennis, *Ibid.*, 2039; cf. Tressler and Dennis, *J. Phys. Ch.*, **31**, 1429 (1927).

scale). Experiments have been made with Ge-Al alloys, also with glass in which the Si was replaced with Ge.

2. Occurrence. — Germanium is found to the extent of about 0.01% as an impurity in many sulfide ores. It occurs (5%–7%) in argyrodite, $3Ag_2S \cdot GeS_2$, which is mined at Freiberg, Saxony, and Ormo, Bolivia. Enargite contains up to 0.1% Ge.[1] Many other ores (zinc blende, cassiterite, stannite, pyrargyrite, etc.) carry traces of this element. There is practically no active market for the metal. Recent quotations have been \$8–\$12 per gram.

3. Preparation. — Germanium may be obtained by reduction of the oxide, GeO_2, with H, C, or Mg°; also by reduction of the sulfide in hydrogen.[2]

4. Oxides and Hydroxides. — Germanium forms two oxides, GeO and GeO_2, the latter being the more stable. GeO is a dark gray powder obtained by heating $Ge(OH)_2$ in an inert atmosphere. It is distinctly volatile. Germanous hydroxide, $Ge(OH)_2$, yellow, precipitates when Ge^{++} is treated with NaOH. It is soluble in excess of the reagent, is yellow when first formed, but turns red on heating, and as an acid is slightly weaker than acetic acid. Germanic oxide, GeO_2, white, is formed upon ignition of Ge°, GeS_2, etc.[3] The corresponding hydroxide apparently has not been prepared.

5. Solubilities. — *a. Metal.* — Germanium is insoluble in H_2O and HCl, soluble in aqua regia and H_2SO_4, reacts with HNO_3 to form GeO_2, and combines directly with the halogens. It is insoluble in NaOH solution but dissolves with incandescence in the fused alkalis.

b. Oxides. — Germanous oxide, GeO, dissolves readily in HCl or NaOH. Germanic oxide,[4] GeO_2, is slightly soluble in H_2O or acids. Fused with a fixed alkali hydroxide or carbonate, it is converted into a water-soluble germanate.

c. Salts. — The halogen salts of Ge^{+4} are decomposed by H_2O. If a solution of the oxide in excess of HCl is evaporated to dryness the Ge is all volatilized. The sulfides, GeS, red, and GeS_2, white, are slightly soluble in H_2O, soluble in alkali sulfides and hydroxides, insoluble in HCl or H_2SO_4, soluble in aqua regia with separation of sulfur. Nitric oxide changes GeS_2 to GeO_2 with oxidation of the S^{--}.

6. Reactions. — In its general behavior toward reagents germanium lies between silicon and tin. The halogen salts readily hydrolyze in water. The hydroxides are amphoteric. Solutions of Ge^{++} give a yellow precipitate with OH^-, a brown precipitate of GeS with S^{--}, a white precipitate with $Fe(CN)_6^{-4}$. Solutions of Ge^{+4} give no precipitate with OH^- because of the ready conversion to GeO_3^{--}. H_2S forms a white precipitate of GeS_2, readily soluble in $(NH_4)_2S$.[5]

7. Ignition. — Compounds of Ge heated before the blowpipe, in the reducing flame without an alkaline flux, form the metal, and at the same time a white coating of the oxide. Ge forms a colorless bead with borax. The spark spectrum shows a characteristic blue line at 468.6mμ.[6, 7] Certain of the sulfide ores heated in an atmosphere of H_2S or illuminating gas produce an orange yellow sublimate (like Sb) having characteristic microscopic crystals.[8]

8. Detection. — Germanium is precipitated as the sulfide in Group II and detected in the $(NH_4)_2S_x$ extract.[9] See 6 and 7 above.

[1] Papish, *et al.*, *J. Am. Ch. Soc.*, **49**, 3031–2 (1927).

[2] Tressler and Dennis, *loc. cit.* Müller, *et al.*, *Proc. Am. Phil. Soc.*, **65**, 15 (1926); Thomas and Pugh, *J. Ch. Soc.*, **125**, 816 (1924).

[3] Concerning the preparation of pure GeO_2, see Dede and Russ, *Ber.*, **61B**, 2451 (1928), *C.A.* **23**, 1360.

[4] Pugh, *J. Ch. Soc.*, **1929**, 1537–41, *C.A.* **23**, 5362.

[5] For a survey of the work on Ge at Cornell University, 1921–7, see Dennis, *Z. anorg. allgem. Ch.*, **174**, 97–141 (1928). For a brief bibliography, see Bur. Mines I. C. 6401, 13–4 (1930).

[6] Papish, *Ch. News*, **124**, 3 (1922).

[7] Geilmann and Brünger, *Z. anorg. allgem. Ch.*, **196**, 312–20 (1931), *C.A.* **25**, 2937, detected spectroscopically 0.25γ Ge in 0.025 cc. of solution.

[8] Haushofer, *Sitzungsber. Münch. Acad.*, **1887**, 133, *Ch. Zentr.* **59**, 867 (1888).

[9] Cf. Noyes and Bray, p. 62; Müller, *J. Am. Ch. Soc.*, **43**, 2549 (1921); Wada and Kato, *Sci. Papers, Inst. P. Ch. Research*, **3**, 243–61 (1925), *C.A.* **20**, 1574; Browning and Scott, *Am. J. Sci.*, **44**, 313–5 (1917), *C.A.* **11**, 3190.

9. Determination. — Germanium may be separated as $GeCl_4$ by distillation,[1] precipitated as the sulfide, GeS_2, ignited to the oxide, GeO_2, and weighed as such.[2] Germanium may be precipitated as Mg_2GeO_4 from an ammoniacal solution, ignited and weighed as such. This method is similar to the phosphate method for Mg, etc.[3]

10. Oxidation and Reduction. — If Zn° is added to an acid solution of Ge^{+4}, the metal, Ge°, is precipitated as a dark brown slime. If GeS_2 is heated in a current of H_2, GeS is first formed and finally Ge°.

§112. Tellurium (L. *tellus* = earth). Te = 127.5. Atomic No. 52. Valence 2 4 and 6. Discovered by Reichenstein in 1782.

1. Physical Properties. — Density, 6.225;[4] melting point, 453° (in vacuum);[5] boiling point, 1390°. Tellurium is crystalline, silvery white, semimetallic, brittle, stable in air and in boiling H_2O. Heated in the air it burns with a greenish flame. In its general properties and reactions it is closely related to S and Se. Tellurium has been called "the useless metal." It is, however, used to a slight extent in ceramics.

2. Occurrence. — A small amount of native tellurium has been found. It occurs chiefly, however, as a telluride in Hungary, the United States (Colorado), and various parts of South America and Japan. Some of the minerals are: tellurite, TeO_2; tetradymite, Bi_2Te_2S; melonite, Ni_2Te_3; coloradoite, HgTe. Tellurium is found, as an impurity, in sulfur (Japanese), in gold and silver ores, in the anode sludge of copper refineries, etc. During 1929 less than 1000 pounds were sold. The price was 15¢–18¢ per ounce.

3. Preparation. — There are a number of methods for obtaining Te° each satisfactory for a type of raw material. (a) Fusion with Na_2CO_3 and C converts Te into a telluride, as Na_2Te; then solution in H_2O in the absence of air, filtration, and air oxidation gives Te° as a gray metallic powder. Any Se originally present will be precipitated also. (b) Anode sludge is roasted in air to form TeO_2. This is condensed and reduced to Te° by smelting with charcoal. (c) Heating in a current of Cl_2 gives $TeCl_4$, which is volatile. The distillate is collected in H_2O causing decomposition of the chloride to H_2TeO_3 from which Te° may be precipitated by a bisulfite. The purification of Te° is not an easy task.[6]

4. Oxides and Hydroxides. — Three oxides have been reported, TeO, TeO_2 and TeO_3. Tellurium monoxide is said to be formed by heating $TeSO_3$ in a vacuum above 180°: $TeSO_3 = TeO + SO_2$.[7] The product is somewhat unstable, oxidizing slowly to TeO_2 in moist air or when heated in dry air. Tellurium dioxide, TeO_2, forms when Te° is burned in the air and when $TeCl_4$ is decomposed by boiling H_2O; is a white crystalline solid, very slightly soluble in H_2O (forming tellurous acid, H_2TeO_3), more soluble in acids[8] from which dilution with H_2O precipitates TeO_2 or H_2TeO_3. Tellurous acid is formed when a solution of Te in HNO_3 is poured into cold H_2O. Warming to 40° changes the product to TeO_2. When heated TeO_2 fuses at a low red heat to form a yellow liquid. Volatilization

[1] Browning and Scott, *Am. J. Sci.*, **46**, 663–5 (1918), *C.A.* **13**, 17.

[2] Dennis and Johnson, *J. Am. Ch. Soc.*, **45**, 1380 (1923); Dennis and Papish, *Ibid.*, **43**, 2140 (1921); James and Fogg, *Ibid.*, **51**, 1459–60 (1929).

[3] Müller, *J. Am. Ch. Soc.*, **44**, 2493 (1922).

[4] Slattery, *Phys. Rev.*, [2] **25**, 333 (1925).

[5] Damiens, *Compt. rend.*, **174**, 1344 (1922). Simek and Stehlik, *Coll. Czechoslov. Ch. Communications*, **2**, 303–14 (1930), *C.A.* **24**, 4228, obtained 452.0° with "spectroscopically pure" Te.

[6] See Friend VII, 2, 352.

[7] Damiens, *Compt. rend.*, **179**, 829 (1924), says that the product is a mixture of Te and TeO_2.

[8] For the reaction between TeO_2 and HCl between 0° and 170° see Parker and Robinson, *J. Ch. Soc.*, **1928**, 2853–7, *C.A.* **23**, 1074.

occurs above 400°. This property is, however, more pronounced in the metal itself. H_2TeO_4 is made by fusing TeO_2 with $NaNO_3$, treating the Na_2TeO_4 thus obtained with Pb^{++} or Ba^{++} and decomposing the salt with H_2SO_4. Telluric acid, $H_2TeO_4 \cdot 2H_2O$, separates in the form of colorless crystals upon evaporation and addition of alcohol. The same compound may be obtained by oxidation of $TeCl_4$ with $HClO_3$ followed by addition of concentrated HNO_3 to precipitate the desired product.[1] It can be recrystallized from H_2O. Upon heating above 3600°, it forms TeO_3, orange yellow. The trioxide is readily reduced to TeO_2.

5. Solubilities. — *a. Metal.* — Te° is insoluble in HCl. Aqua regia and HNO_3 oxidize it to H_2TeO_4. In H_2SO_4 it becomes H_2TeO_3 with evolution of SO_2. It is soluble in warm concentrated cyanide, from which HCl precipitates Te°. Solutions of alkali hydroxides dissolve Te°. All of the halogens combine with Te° to form halides.

b. Oxides. — TeO_2 is very slightly soluble in H_2O, soluble in acids and the alkali hydroxides. The trioxide is insoluble in H_2O, in HNO_3, and in cold HCl. Hot concentrated solutions of alkali hydroxides dissolve TeO_3 with formation of TeO_4^{--}. Tellurous acid is slightly soluble in H_2O, insoluble to soluble in NaOH depending on the mode of preparation. Telluric acid, $H_2TeO_4 \cdot 2H_2O$, is readily soluble in H_2O, less soluble in HNO_3 or alcohol.

c. Salts. — Halide salts of Te, e.g., $TeCl_4$, hydrolyze in H_2O. Solutions of the alkali tellurites and tellurates form precipitates with ions of the metals; e.g., $Na_2TeO_4 + BaCl_2 = BaTeO_4 + 2\ NaCl$.

6. Reactions. — Tellurium is classed with the Group II metals because of its precipitation from solutions of TeO_3^{--} or TeO_4^{--} by H_2S. The precipitate is not a sulfide,[2] but is Te° mixed with S°. In appearance the precipitate resembles SnS and is readily soluble in $(NH_4)_2S$. At a high temperature Te° and H_2 unite directly forming hydrogen telluride,[3] H_2Te. It is a colorless gas with an odor similar to H_2S, burns with a blue flame, is fairly soluble in H_2O and is precipitated as Te° from solution by atmospheric oxygen. H_2Te precipitates from solution ions of metals as does H_2S and H_2Se. Tellurate ion, TeO_3^{--}, treated with KI in dilute acid, gives a black precipitate of TeI_4 that dissolves in excess reagent, forming red TeI_6^{--} (distinction from Se) (cf. 8 and 10).

7. Ignition. — Tellurium combines, on ignition, with most metals to form tellurides. TeO_3, ignited, decomposes to TeO_2 and O_2. All compounds of Te when fused with $NaNO_3$ give Na_2TeO_4. All Te compounds give, on charcoal with the blowpipe, a white powder that colors the reducing flame green. Heated in an open glass tube, Te compounds give a sublimate of TeO_2 that melts upon heating. Te compounds fused with KCN in a current of H_2 form the tellurocyanate, KCNTe, soluble in H_2O but precipitated by air as Te° (distinction and separation from Se). Heated with Na_2CO_3 on charcoal, Te compounds give Na_2Te. This blackens Ag with formation of Ag_2Te.

8. Detection. — Reduction to Te° in slightly acid solution by SO_2 offers an easy means for separating Te from many other metals, especially Se which is precipitated from concentrated acid solution, Te only from dilute. The tellurium may be dissolved after filtration, and the solution tested with KI (cf. 6). A very delicate test for Te involves reduction with $TiCl_3$. The H_2Te evolved is decomposed to form a mirror as in the Marsh test for As.[4]

9. Determination.[5] — *Gravimetrically*, a telluride may be heated in a current of Cl_2, the volatile $TeCl_4$ collected in H_2O and precipitated as Te° by SO_2 or hydroxylamine hydrochloride. The metal is filtered off, dried at 110° (preferably in an inert atmosphere) and weighed. Tellurites or tellurates may be treated in the same way, except that HCl is substituted for Cl_2. If Se is present it will volatilize as Se_2Cl_2 and accompany the $TeCl_4$. A separation may be effected by distilling the Se from a $HCl-H_2SO_4$ solution[6] or precipitating the Se from 5 *N* HCl solution by hydroxylamine hydrochloride. In

[1] Cf. Damiens, *Compt. rend.*, **174**, 1344, 1548 (1922). Meyer, *et al.*, *Z. anorg. allgem. Ch.*, **119**, 132 (1921).

[2] Hageman, *J. Am. Ch. Soc.*, **41**, 329 (1919).

[3] Moser and Ertl, *Z. anorg. allgem. Ch.*, **118**, 269 (1921).

[4] Tomicek, *Bull. soc. ch.*, **41**, 1399–403 (1927), *C.A.* **22**, 366.

[5] Cf. Lenher, *Proc. Am. Phil. Soc.*, **65**, 33–50 (1926), *C.A.* **20**, 2801.

[6] Lenher and Smith, *Ind. Eng. Ch.*, **16**, 837 (1924).

either case the Te is left in the residual liquid and may be determined as above. *Volumetrically,* Te may be determined by oxidation with excess of standard dichromate and titration of the excess, using $FeSO_4$ (Se apparently does not interfere). Various iodometric methods have been suggested but Se interferes in practically all of them.

10. Oxidation and Reduction. — Hydrogen at high temperatures reduces Te to H_2Te. H_2S reduces Te compounds to Te°. Fusion with $NaNO_3$ oxidizes all Te compounds to Na_2TeO_4. SO_2 and hydroxylamine hydrochloride in dilute acid solution reduce Te compounds to Te°. $SnCl_2$ and Zn° in acid solutions give, with Te compounds, a black precipitate of Te°. Tellurates boiled with HCl evolve Cl_2 and are reduced to H_2TeO_3, which precipitates as TeO_2 on adding H_2O (distinction from Se).

§113. Selenium.[1] (Gr. *selene* = moon). Se = 79.2. Atomic No. 34. Valence 2, 4 and 6. Discovered by Berzelius in 1817.

1. Physical Properties. — Density, of the red variety, 4.50 at 25°; of the gray variety, 4.84;[2] melting point, of the gray variety, 220.2° ± 0.5°;[3] boiling point, 690°. Selenium occurs in at least four allotropic forms:[4] one, amorphous, vitreous and black in color obtained by rapidly cooling the liquid (this form, finely powdered, appears red); two crystalline monoclinic forms, red in color, fairly stable below 100° but changing above 120° to the most stable crystalline, gray, " metallic " selenium, that melts at 220° and is insoluble in carbon bisulfide. All other forms gradually change to the gray, the rate depending upon thermal conditions. When Se is heated on charcoal the vapor evolved has a distinctly unpleasant odor. The electrical conductivity of Se (gray especially) is very low at room temperature or in the dark, but exposure to light or increase in temperature causes a marked lowering of resistance. This property is the basis for the action of the selenium photoelectric cell which is so sensitive that, under proper conditions, the light from a star will produce an appreciable effect.[5] The principal uses for selenium are: in the glass industry to produce various colored glasses (especially a ruby red), in fire-proofing electric cables, and in the rubber industry.[6]

2. Occurrence. — Selenium is a relatively rare element. It is found generally in pyrites and sulfide ores as well as in native sulfur. Selenides of the heavy metals, especially Cu, Ag and Pb, also selenites of Cu, Co and Pb are found to a limited extent in South America, Mexico, the United States, and elsewhere. During the year 1929 about 325,000 lbs. of Se were sold at an average price of $2.18 per pound.[7]

3. Preparation. — The chief source of Se is the lead chamber " mud " of sulfuric acid plants, where it is found as a red deposit mixed with some S, As_2O_3, Sb_2O_3, $PbSO_4$, etc. Other (potential) sources are the anode sludge of electrolytic copper refineries and the flue dust of the sulfur burners in H_2SO_4 plants. The methods for recovery of Se vary in detail, but in general they involve oxidation to selenous acid and decomposition of this compound in fairly concentrated acid solution with SO_2. The precipitated Se° is removed by filtration, dried and distilled. The purified product contains less than 1% impurities and is usually free from Te.

4. Oxides and Hydroxides. — Selenium forms one oxide that has been well established, namely selenium dioxide, SeO_2; others have been described, as Se_2O_3, Se_3O_4 and

[1] For a bibliography on selenium see: Marion F. Doty, " Selenium, a list of references, 1817–1925." New York Public Library, **1927**.

[2] Slattery, *Phys. Rev.*, [2] **25**, 333 (1925).

[3] Berger, *Z. anorg. allgem. Ch.*, **85**, 75 (1914).

[4] Cf. Briegleb, *Naturwissenschaften*, **17**, 51 (1929), *Z. physik. Ch.*, **144**, A, 321–58 (1929); *C.A.* **23**, 1788.

[5] Cf. Friend VII, 2, p. 297–8.

[6] Somerville and Ball, *Rubber Age*, **24**, 490–4 (1929), *C.A.* **23**, 1774.

[7] Mineral Ind., **1929**, p. 698.

SeO_3,[1] but they need further investigation. Selenium dioxide is prepared by burning the metal.[2] A very pure product results by conducting the reaction in a mixture of NO_2 and O_2. Colorless crystals are obtained that sublime readily, have a disagreeable odor, are hygroscopic, and melt to an orange-yellow liquid when heated above 340°. The vapor is yellowish green. Selenous acid, H_2SeO_3, is prepared by dissolving SeO_2 in H_2O, or oxidizing Se° with HNO_3, aqua regia, etc. It may be recovered in crystalline form by evaporation at a low pressure over H_2SO_4. Selenic acid, H_2SeO_4, is conveniently prepared by oxidation of H_2SeO_3 with $HClO_3$.[3] Purification is effected by addition of $BaCl_2$, filtration to separate the precipitated $BaSeO_4$ and removal of the Ba^{++} with H_2SO_4. The crystals, secured by evaporation, melt at 58°. At least two hydrates have been reported that melt much lower.

5. Solubilities. — *a. Metal.* — Se° appears to dissolve[4] in cold concentrated H_2SO_4 without oxidation, to give a green colored liquid (dilution with H_2O precipitates the Se°). If the liquid is warmed SO_2 is evolved and the color disappears, the Se° being oxidized to SeO_2. Aqua regia and HNO_3 oxidize Se° to SeO_2.

b. Oxides. — Selenous oxide, SeO_2, is readily soluble in H_2O forming H_2SeO_3. Selenic acid, H_2SeO_4, is also readily soluble in H_2O.

c. Salts. — The selenites and selenates of the alkaline earth metals are insoluble and may be precipitated by adding the metal ion to a neutral solution of an alkali selenite or selenate, $Na_2SeO_3 + BaCl_2 = BaSeO_3 + 2\ NaCl$. Many of the selenites are soluble in excess of the acid. Selenates are less stable than selenites. $BaSeO_4$ is soluble in HCl (distinction and separation from $BaSO_4$) because upon boiling it is reduced to $BaSeO_3$. Salts in which Se forms the positive ion, e.g., $SeCl_4$, hydrolyze readily in contact with H_2O.

6. Reactions. — Selenous acid treated with H_2S forms a precipitate of Se° and S, lemon yellow, becoming bright red on heating. This mixture is soluble in $(NH_4)_2S$, hence Se is classed with the arsenic division of Group II while because of its general properties it belongs with sulfur. Se° and H_2, when heated together, begin to combine directly at 250°, forming H_2Se. The same compound is obtained by treating K_2Se, FeSe, etc., with dilute HCl or H_2SO_4. HNO_3 gives H_2SeO_3 with selenides. H_2Se is a colorless gas with an odor similar to H_2S but more penetrating. It is more poisonous and more soluble in H_2O than H_2S. Its aqueous solution reacts acid and, on standing, red flakes of Se° are deposited. It precipitates the selenides of the metals, having almost the same solubilities as the corresponding sulfides. Soluble sulfites react with H_2Se to form Se° and S. Sn^{++}, Fe^{++}, H_3PO_3, H_3PO_2, or hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) reduce selenites to Se°, red, changing to the gray form on warming. KI reduces either SeO_3^{--} or SeO_4^{--} to Se°.

7. Ignition. — When Se° or a Se compound is fused with KCN in a current of H_2, potassium selenocyanate, KCNSe, is formed. Long boiling with HCl separates Se°, but this does not take place on exposure of the solution to the air (separation from Te). Selenium compounds heated on charcoal with Na_2CO_3 are changed to Na_2Se, which yields a black satin stain with Ag°, and H_2Se with dilute acids.

8. Detection. — If present as the selenide the sample may be decomposed by HCl or H_2SO_4, forming H_2Se, which is (a) conducted into water and Se° precipitated by passing air through the solution, or (b) treated as in the Marsh test for As. If a large amount of Se is present the " mirror " will be red; a small quantity gives a deposit closely resembling that formed by arsenic.[5] Should the presence of As be suspected, a preliminary separation is necessary (see above). Se, in solution, may be detected by reduction to Se° with hydrazine in warm H_2SO_4 solution. A red color or precipitate indicates the presence of the element. The test will reveal 5 mg. of Se per liter of solution. In case

[1] Cf. Worsley and Baker, *J. Ch. Soc.*, **123**, 2870 (1923).
Braun, *Metallbörse*, **19**, 2806–7, 2862–3 (1929), *C.A.* **24**, 1811.

[2] Meyer, *Ber.*, **55B**, 2082 (1922).

[3] Meyer and Moldenhauer, *Z. anorg. allgem. Ch.*, **116**, 193–200 (1921), *C.A.* **15**, 2397. Cf. Manchot and Wirzmüller, *Z. anorg. allgem. Ch.*, **140**, 47–51 (1924), *C.A.* **19**, 792; Dennis and Koller, *J. Am. Ch. Soc.*, **41**, 949 (1919).

[4] It may actually be a colloidal solution.

[5] Meunier, *Compt. rend.*, **163**, 332–4 (1916), *C.A.* **11**, 128.

SeO_3^{--} is being tested, SO_2 may be used in place of the hydrazine. After the reduction of SeO_3^{--}, any SeO_4^{--} may be detected by further boiling with HCl.[1] A sample of concentrated H_2SO_4 can be tested for Se by first adding a small amount of bromine water containing some KBr and then distilling. The concentration of H_2SO_4 should not be reduced below 75%. The distillate after reduction of the excess Br_2 with excess $NH_2OH \cdot HCl$ is boiled, whereupon a red color develops if Se is present.[2] If the H_2SO_4 is free from iron addition of codeine phosphate will produce a green color deepening to blue green in a few minutes if there is any Se in the acid. Tellurium retards the appearance of the color.[3]

9. Determination. — *Gravimetrically*, selenium may be separated as $SeBr_4$, by distillation from a solution containing Br_2 and KBr, precipitated as the metal by hydroxylamine hydrochloride, dried at 105°, and weighed. A somewhat similar procedure involves, first, the removal of any HNO_3 from the sample by low temperature evaporation with HCl, which at the same time reduces SeO_4^{--} to SeO_3^{--}. Increasing the HCl concentration to 4 *N*, and introducing SO_2 precipitates the selenium as Se°. This may be dried and weighed as such. Au, Pd, Sb, Bi, Cu, etc., interfere but may be separated by means of HNO_3.[4] *Volumetrically*, selenium may be determined, after the removal of Te, (a) by various modifications of the iodometric method, e.g., reduction of the Se with excess standardized $Na_2S_2O_3$ and titration of the excess with iodine; (b) by oxidation with excess $KMnO_4$ and titration of the excess with oxalic acid or Fe^{++}.

10. Oxidation and Reduction. — Se° is oxidized to SeO_2 by HNO_3, aqua regia, hot concentrated H_2SO_4, ignition in air, etc. H_2SeO_3 is oxidized to H_2SeO_4 by chlorination, or by fusion with a nitrate. H_2SeO_4 is reduced to H_2SeO_3 by heating with HCl. Hydrazine, hydroxylamine, H_2S, SO_2, etc., reduce SeO_3^{--} to Se° in acid solution (cf. 6).

THE IRON GROUP (THIRD GROUP)

ALUMINUM, CHROMIUM, IRON

§124. Aluminum (L. *alumen* = alum). Al = 26.97. Atomic No. 13. Valence 3. Isolated by Oersted in 1824.

1. Physical Properties. — Density, 2.70;[5] melting point, 658.7°;[6] boiling point, 1800°.[7] Aluminum is a tin white metal (the powder is gray), odorless and tasteless, very ductile and malleable, about as hard as silver. As a conductor of heat it is about half as good as copper, i.e., 0.502 cal. per second. Its electrical conductivity is about 60% as good as copper, considered per unit of cross-sectional area, but weight for weight its conductivity is twice that of copper. Commercially "pure" aluminum contains slightly over 99% Al and has properties that are considerably different from those of

[1] Müller, *Z. physik. Ch.*, **100**, 346 (1922).
[2] Noyes and Bray, p. 323.
[3] Raikhinstein, *Trans. Inst. Pure. Ch. Reagts.* (Moscow), **1927**, No. 6, 27–30, *C.A.* **23**, 2391. Schmidt, *Arch. Pharm.*, **252**, 161–5 (1914), *C.A.* **8**, 2990.
[4] Cf. Hillebrand and Lundell, p. 260.
[5] Edwards, *Trans. Am. Electroch. Soc.*, **47**, 295 (1925).
[6] B. Stds. Cir. 35; cf. Edwards, *loc. cit.*, p. 289.
[7] Mott, *Trans. Am. Electroch. Soc.*, **34**, 255 (1918).

especially refined samples having a purity above 99.85%.[1] The chief uses of aluminum at the present time are for automobile parts, cooking utensils, a deoxidizer in steel manufacture, and electrical conductors. The most important alloy is the so-called No. 12, which is about 92% Al and 8% Cu. Duralumin contains about the same percentage of Al, half as much Cu, and 0.75% each of Mg and Mn.[2]

2. Occurrence. — While not found free in nature, aluminum is, relatively, one of the most abundant elements, comprising about 7.8% of our lithosphere.[3] It is found as a silicate, the major component of all clays, in feldspars, e.g., $K_2Al_2SiO_6$, in cryolite, Na_3AlF_6, but by far the most important source, from an industrial standpoint, is bauxite, a hydrated aluminum oxide, $Al_2O(OH)_4$. The world's production of this ore is about 1.7 million tons per year, of which France produces about one-third; the United States (Arkansas, Georgia, Alabama, Mississippi), one-fourth; Hungary, the Guianas and Italy the balance.[4] The current price of metallic aluminum is 20–25 cents per pound.

3. Preparation. — Since it has been found impractical[5] to purify metallic aluminum, the bauxite is first carefully purified by the Bayer process, which involves a preliminary roasting of the ore, followed by digestion with strong sodium hydroxide. The sodium aluminate solution thus obtained is freed from iron by dilution and subsequently the aluminum hydroxide is precipitated. The precipitate is dried and subjected to electrolysis in a bath of molten cryolite, at a temperature of 1000° (Hall process). The liquid aluminum collects in a pool at the bottom of the cell, is removed at intervals and cast into pigs or fabricated into sheets, etc.[6]

4. Oxides and Hydroxides. — Aluminum oxide, Al_2O_3, is formed by heating the hydroxide, nitrate, acetate or other organic salt. The ignited oxide is difficultly soluble in acids but may be dissolved after fusion with alkali bisulfate or carbonate.[7] Aluminum hydroxide is precipitated when solutions of aluminum salts are treated with NH_4OH. In the cold the product is $Al(OH)_3$ or $(Al_2O_3 \cdot 3H_2O)$; when hot, $HAlO_2$ (or $Al_2O_3 \cdot H_2O$).

5. Solubilities. — *a. Metal.* — Pure aluminum is scarcely oxidized in dry or moist air; the powder, however, oxidizes gradually. Powdered or leaf aluminum when boiled with water, evolves hydrogen, forming the hydroxide. The metal is attacked by the halogens, forming the corresponding halide. Dilute H_2SO_4 attacks Al° slowly, evolving hydrogen; the hot, concentrated acid dissolves it readily, with evolution of SO_2. Nitric acid produces passivity, but in the presence of small amounts of other ions, e.g., Hg^{++}, rapid solution is effected with evolution of NO in the concentrated acid, and formation of NH_4NO_3 in the dilute acid. Hydrochloric acid, dilute or concentrated, dissolves aluminum readily, with evolution of H_2. Fixed alkalis readily produce a solution of the corresponding aluminate: $2\,Al + NaOH + 2\,H_2O = 2\,NaAlO_2 + 3\,H_2$. Al° is also attacked by the fixed alkali carbonates. When ignited with Na_2CO_3, aluminum oxide is formed and the sodium may be vaporized. Aluminum is not appreciably attacked by cold, dilute acetic acid; boiling increases the rate to approximately 3 g. per square meter per hour.[8]

b. Oxide and Hydroxide. — The oxide, Al_2O_3, is insoluble in water, and when not too strongly ignited, dissolves readily in dilute acids and in fixed alkalis. Corundum, crystallized Al_2O_3, is insoluble in acids, but is rendered soluble by fusion in fixed alkali car-

[1] Edwards, *loc. cit.*, discusses some properties of this latter grade.

[2] Cf. *A. S. T. M. Standards*, **1924**, p. 451; *Tentative Standards*, **1930**, p. 98.

[3] Clarke, "Data of Geochemistry," U. S. Dept. of the Interior, Washington, **1920**, p. 35.

[4] Mineral Ind., **1928**, p. 21.

[5] Cf. Edwards, *loc. cit.*

[6] Stoughton and Butts, "Engineering Metallurgy," McGraw-Hill Book Company, New York, **1926**, p. 329–32.

[7] Britton, *J. Ch. Soc.*, **127**, 2133 (1925), says it is remarkable that while alumina is one of the few oxides that can be considered amphoteric in solution, it should be the only one definitely amphoteric in the dry state, yielding on fusion with alkali or alkali metal carbonates products that are soluble.

[8] Hamlin and Turner, "Chemical Resistance of Engineering Materials," Chemical Catalog Co., New York, **1923**, p. 68.

bonates or sulfates. The hydroxide, $Al(OH)_3$, is insoluble in water, readily soluble in acids and fixed alkalis, sparingly soluble in NH_4OH, the solubility being much lower in the presence of ammonium salts, due to lowering of the $[OH^-]$.

c. Salts. — Aluminum phosphate is the most important salt, insoluble in water; the normal acetate is soluble, the basic acetate, $Al(OH)_2C_2H_3O_2$, insoluble. The chloride is deliquescent. The double sulfates of aluminum and the alkali metals (alums, $MAl(SO_4)_2 \cdot 12H_2O$) are soluble and readily melt in their water of crystallization. Anhydrous aluminum sulfate is insoluble in water. Solutions of normal salts of aluminum have an acid reaction due to hydrolysis.

6. Reactions. — *a.* The alkali hydroxides[1] and carbonates precipitate aluminum hydroxide, $Al(OH)_3$ (Eq. 1), colorless to grayish-white, gelatinous, insoluble in water, soluble in excess of the fixed alkali hydroxides to form $MAlO_2$[2] (Eq. 2), sparingly soluble in the fixed alkali carbonates and in NH_4OH, but much less so if ammonium salts be present (see above). The solution of fixed alkali aluminate yields a precipitate of $Al(OH)_3$ by careful neutralization of the alkali with acids, including H_2S (Eq. 3), and H_2CO_3; treating with excess NH_4Cl[3] produces the same result (Eq. 4), except that $[OH^-]$ is reduced by combination with NH_4^+ (forming the slightly ionized and unstable NH_4OH, readily removed as NH_3 by heating, Eq. 5). The precipitate is more compact and is washed more readily than that obtained by neutralization of an acid solution. $BaCO_3$ on digestion in the cold for some time, completely precipitates Al^{+3} as the hydroxide (Eq. 6), mixed with a little basic salt (see §**126**, 6, *a*). The presence of citric, oxalic or tartaric acid greatly hinders the precipitation of $Al(OH)_3$, and an excess may entirely prevent its precipitation by the formation of a complex ion. Organic substances may be removed by addition of Na_2CO_3 and $NaNO_3$, evaporation to dryness, and ignition of the residue.

$$(1)\ AlCl_3 + 3\ NaOH = Al(OH)_3 + 3\ NaCl$$
$$2\ AlCl_3 + 3\ Na_2CO_3 + 3\ H_2O = 2\ Al(OH)_3 + 6\ NaCl + 3\ CO_2$$

$$(2)\ Al(OH)_3 \rightleftarrows H_3AlO_3 \rightleftarrows HAlO_2 + H_2O$$
$$HAlO_2 + NaOH = NaAlO_2 + H_2O$$

$$(3)\ 2\ NaAlO_2 + H_2S + H_2O = 2\ Al(OH)_3 + Na_2S$$

$$(4)\ NaAlO_2 + NH_4Cl + H_2O = Al(OH)_3 + NH_3 \uparrow + NaCl$$

$$(5)\ NaOH + NH_4Cl + \text{heat} = NH_3 \uparrow + NaCl + H_2O$$

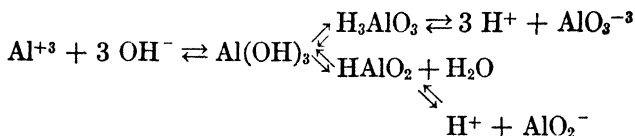
$$(6)\ 2\ AlCl_3 + 3\ BaCO_3 + 3\ H_2O = 2\ Al(OH)_3 + 3\ BaCl_2 + 3\ CO_2$$

[1] For precipitation with NH_4OH, see: Jander and Ruperti, *Z. anorg. allgem. Ch.*, **153**, 253–9 (1926).

[2] Cf. Goudriaan, *Rec. trav. ch.*, **41**, 82–95 (1922); Fricke, *Z. Elektroch.*, **28**, 357–8 (1922).

[3] $(NH_4)_2SO_4$ gives a precipitate more easily filtered.

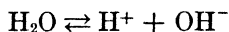
Considering the aluminum hydroxide system in a broader way:

$$Al^{+3} + 3\ OH^- \rightleftarrows Al(OH)_3 \begin{cases} \rightleftarrows H_3AlO_3 \rightleftarrows 3\ H^+ + AlO_3^{-3} \\ \rightleftarrows HAlO_2 + H_2O \\ \qquad \rightleftarrows H^+ + AlO_2^- \end{cases}$$

If OH^- is added to Al^{+3}, then $Al(OH)_3$ or $AlO_2^-(AlO_3^{-3})$ will be produced, the amount depending upon the hydroxyl ion concentration, i.e., with a small amount of OH^-, the main product will be $Al(OH)_3$, with excess of hydroxyl ion, AlO_2^- will predominate (cf. 4). Conversely, H^+ added to $AlO_2^-(AlO_3^{-3})$ produces $Al(OH)_3$ or Al^{+3}. Obviously in either case the addition of one ion accomplishes the same result as the removal of the other. Introduction of OH^- is the same as removal of H^+ and vice versa.

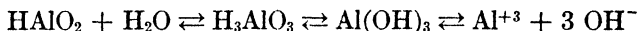
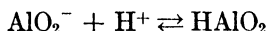
An application of this theory may be of value. The action of NH_4Cl (Eq. 4, above) may be formulated as follows:

$$NaAlO_2 \rightleftarrows Na^+ + AlO_2$$

$$NaOH \rightleftarrows Na^+ + OH^-\text{[1]}$$

$$H_2O \rightleftarrows H^+ + OH^-$$

Since for a stable state all reactions must be in equilibrium:

$$AlO_2^- + H^+ \rightleftarrows HAlO_2$$

$$HAlO_2 + H_2O \rightleftarrows H_3AlO_3 \rightleftarrows Al(OH)_3 \rightleftarrows Al^{+3} + 3\ OH^-$$

The introduction of: $NH_4Cl \rightleftarrows NH_4^+ + Cl^-$, makes possible $NH_4^+ + OH^- \rightleftarrows NH_4OH$. Upon heating, $NH_4OH \rightarrow NH_3 \uparrow + H_2O$. Thus the $[OH^-]$ is reduced and this brings about further combining of H^+ and AlO_2^- to produce more H_3AlO_3 than will stay in solution; hence the precipitation of H_3AlO_3, i.e., $Al(OH)_3$.

b. Oxalates do not precipitate Al^{+3}. The acetate is decomposed upon boiling, forming the insoluble basic acetate (separation of Fe and Al from Group IV): $Al(C_2H_3O_2)_3 + 2\ H_2O = Al(OH)_2(C_2H_3O_2) + 2\ HC_2H_3O_2$. The basic acetate is best formed as follows: to the solution of Al^{+3}, add Na_2CO_3 or $(NH_4)_2CO_3$ sufficient to neutralize any excess acid, but not enough to form a precipitate. Next add an excess of sodium or ammonium acetate, dilute to 100 cc. or more and boil for some time. Filter while hot, for a reversal of the reaction takes place upon cooling.

Sodium cyanide precipitates $Al(OH)_3$ from solutions of Al^{+3}. Potassium ferrocyanide slowly produces in the cold, more rapidly upon heating, a white precipitate that gradually turns green. Phenylhydrazine, $C_6H_5NHNH_2$, completely precipitates aluminum as $Al(OH)_3$ from a

[1] This furnishes the excess hydroxyl ions, making the system alkaline.

neutral solution of Al^{+3} (complete separation of Al and Cr from Fe, which should be in the Fe^{++} state).[1]

d. Alkali phosphates, e.g., Na_2HPO_4, precipitate aluminum phosphate, $AlPO_4$, white, insoluble in H_2O and acetic acid, soluble in mineral acids and in the fixed alkalis (separation from $FePO_4$). Al^{+3} may be separated from PO_4^{-3} by dissolving in HCl, adding tartaric acid, NH_4OH, magnesia mixture, and digesting some time. The precipitate is $MgNH_4PO_4$. The tin method may also be used. It has the advantage that excess Sn is more easily removed than tartaric acid.

e. The sulfide of aluminum cannot be prepared in the wet way; that prepared in the dry way undergoes complete hydrolysis on exposure to water. H_2S does not precipitate Al^{+3} from acid or neutral solution; from alkaline solutions containing AlO_2^-, hydrosulfic acid precipitates $Al(OH)_3$ if sufficient is added to neutralize the alkali (distinction from Zn, which is rapidly precipitated as ZnS from solutions not too alkaline). The alkali sulfides, e.g., $(NH_4)_2S$, precipitate $Al(OH)_3$; from acid or neutral solutions H_2S is evolved: $2\,AlCl_3 + 3\,(NH_4)_2S + 6\,H_2O = 2\,Al(OH)_3 + 6\,NH_4Cl + 3\,H_2S$; from solutions of AlO_2^-, ammonia is evolved and a fixed alkali sulfide formed: $2\,NaAlO_2 + (NH_4)_2S + 2\,H_2O = 2\,Al(OH)_3 + Na_2S + 2\,NH_3$. Sodium thiosulfate precipitates $Al(OH)_3$ from neutral solutions of Al^{+3}, together with free sulfur and SO_2: $Al_2(SO_4)_3 + 3\,Na_2S_2O_3 + 3\,H_2O = 2\,Al(OH)_3 + 3\,S + 3\,Na_2SO_4 + 3\,SO_2$. Sodium sulfite also precipitates $Al(OH)_3$ with liberation of SO_2: $2\,AlCl_3 + 3\,Na_2SO_3 + 3\,H_2O = 2\,Al(OH)_3 + 6\,NaCl + 3\,SO_2$. Neither of the above reagents precipitates Fe salts, thus effecting a separation of Al (and Cr) from iron.

Aluminum, chromium and ferric sulfates form double salts, called alums, with the alkali sulfates. Perhaps the best known of this group is the so-called common alum,[2] $KAl(SO_4)_2\cdot 12H_2O$. The alums are usually less soluble than their constituent sulfates and may be precipitated by adding a saturated solution of alkali sulfate to a very concentrated solution of Al^{+3}, Cr^{+3} or Fe^{+3} sulfate.

g. Al^{+3} is precipitated by alkali arsenites and arsenates, but not by the corresponding acids.

h. Solutions of alkali chromates and borates precipitate Al^{+3} as $Al(OH)_3$, due to the excess OH^- present in the reagent.

7. Ignition. — Compounds of Al are not reduced to the metal, but most of them are changed to the oxide, by ignition on charcoal. If this residue is moistened with a solution of $Co(NO_3)_2$[3] and again strongly ignited, it assumes a blue color.[4] This test

[1] Hess and Campbell, *J. Am. Ch. Soc.*, **21**, 776 (1899).

[2] Not to be confused with commercial alum, which is crude aluminum sulfate.

[3] Cf. Migliacci and Crapetta, *Ann. ch. applicata*, **17**, 66–74 (1927); Otto, *J. Am. Ch. Soc.*, **48**, 1604–5 (1926).

[4] Gemmill, *et al.*, *J. Am. Ch. Soc.*, **51**, 1165 (1929), have suggested the use of asbestos fibers.

is conclusive only with infusible compounds, and in the absence of colored oxides. Aluminum compounds ignited on charcoal in the presence of sulfur are changed to Al_2S_3.

8. Detection. — After the removal of Groups I and II, aluminum is precipitated with Cr^{+3} and Fe^{+3} as the hydroxide, $Al(OH)_3$, by NH_4OH in the presence of NH_4Cl. It is separated from $Fe(OH)_3$ by warming with NaOH; from $Cr(OH)_3$ by boiling, first with NaOH and H_2O_2 to oxidize CrO_2^- to CrO_4^{--}, then with excess NH_4Cl, which precipitates $Al(OH)_3$. Many of the confirmatory tests applied to this precipitate involve the use of organic compounds. Among the more important is "aluminon," the ammonium salt of aurin tricarboxylic acid.[1] The precipitate of $Al(OH)_3$ is dissolved in 5 cc. of 1 *N* HCl.[2] This solution is treated with 5 cc. of 3 *N* $NH_4C_2H_3O_2$,[3] 5 cc. of a 0.1% solution of the reagent, and after standing a few minutes, with excess NH_4OH containing $(NH_4)_2CO_3$.[4] A bright red precipitate,[5] persisting in the alkaline solution, indicates the presence of aluminum. The test will readily detect 0.3 mg. of Al in the 18–20 cc. volume. Color effects are obtained with much smaller quantities of Al, but 0.3 mg. is about the limit of ready flocculation of the precipitate. Cr does not interfere; Fe is precipitated as $Fe(OH)_3$, reddish brown; many of the rarer elements give red lakes varying in color from that formed by Al.[6] Alizarin red S,[7] 0.1% alcoholic solution, also forms a red color or precipitate with Al^{+3}. The precipitate of $Al(OH)_3$ is dissolved in 1–2 cc. of 5 *N* HCl, then diluted to 5 cc. and 1 cc. of alizarin solution added. NH_4OH is slowly added until the solution is alkaline, i.e., purple in color, boiled 2–3 minutes, cooled and acidified with acetic acid. A bright red color, followed by the separation of a bright red precipitate, indicates the presence of aluminum. The final volume should not exceed 12–15 cc. Silicic acid gives a precipitate of different color. Other metallic hydroxides will not be present at this stage in the regular course of analysis. The reagent is said to detect, immediately, one part of aluminum in 100,000 of water.

Morin, a dyestuff extracted from old fustic, gives a green fluorescence with Al^{+3}. The test is very delicate and is not given by Be and the rare

[1] Hammett and Sottery, *J. Am. Ch. Soc.*, **47**, 142–3 (1925); cf. Yoe and Hill, *J. Am. Ch. Soc.*, **49**, 2395–2407 (1927).

[2] A higher concentration is likely to precipitate the reagent.

[3] Winter, *et al.*, *J. Am. Ch. Soc.*, **51**, 2721–31 (1929), obtained the best results when the test was performed in the presence of 10% $NH_4C_2H_3O_2$, a temperature of 80° for 10 minutes, and a *p*H of about 4.

[4] To prevent interference of alkaline earth metals.

[5] Weiser and Porter, *Fifth Colloid. Symp. Monog.*, **1928**, 369–90, *C.A.* **23**, 1036, have discussed the physical chemistry of color-lake formation.

[6] Middleton, *J. Am. Ch. Soc.*, **48**, 2125–6 (1925).

[7] Atack, *J. Soc. Ch. Ind.*, **34**, 936–7 (1915); cf. Allardyce, *J. Am. Ch. Soc.*, **49**, 1991 (1927); Estill and Nugent, *Ibid.*, **48**, 168–9 (1926); Feigl and Stern, *Z. anal. Ch.*, **60**, 1–43 (1921).

earths.[1] To 5 cc. of neutral Al^{+3} solution, add 1 cc. of morin (0.02 g. per liter of 20% alcohol), shake, and compare with a blank. Excess acid or alcohol interfere.[2]

9. Determination. — *Gravimetrically,* aluminum is (a) precipitated as the hydroxide, ignited to, and weighed as, Al_2O_3;[3] (b) precipitated, dried, and weighed as the phosphate. In (a) and especially where silicate rocks are involved, after removal of SiO_2 the hot solution (66°) is treated first, with NH_4Cl, then dilute NH_4OH until neutral to methyl red (*p*H 6.5), whereupon $Al(OH)_3$, $Fe(OH)_3$, $Ti(OH)_4$, any phosphate, and certain other minor constituents are precipitated. After ignition and weighing, the Fe_2O_3, TiO_2, P_2O_5, etc., are directly determined and subtracted from the total. This gives the amount of Al_2O_3, by difference. There are no satisfactory direct volumetric[4] or electrolytic methods for aluminum.

10. Oxidation and Reduction. — Aluminum is a very active metal, by fusion reducing many elements, in combination, to the metallic state.[5] From solution, Al precipitates Pb, Ag, Hg, Sn, Bi (incompletely), Cu, Cd, Co, Ni, Be (this latter in alkaline mixture only), Tl, Te, Se, Au and Pt in the metallic state; Fe^{+3} is reduced to Fe^{++}. As and Sb in acid solution, e.g., HCl, become AsH_3 and SbH_3, respectively; in alkaline solution, As^{+3} apparently becomes first As° and then AsH_3, As^{+5} is unaffected and Sb^{+3} or Sb^{+5} becomes Sb°. (See Fleitmann test for As.) Al^{+3} is not readily reduced to the metallic state; by fusion with K or Na the metal is obtained, much better, however, by use of the electric current.

§125. Chromium (Gr. *chroma* = color). Cr = 52.01. Atomic No. 24. Valence 2, 3 and 6. Discovered by Vauquelin in 1798.

1. Physical Properties. — Density, 7.138 (25°/4°);[6] melting point, >1700°.[7] Chromium is a crystalline metal about the color of silver, though slightly more grayish. It is not appreciably ductile or malleable and is non-magnetic. It burns to the oxide, Cr_2O_3, when heated to 200–300° in air. Its chief uses are for (1) chrome and chrome nickel steels, less than 1% greatly increasing the hardness, (2) making steel rust-

[1] Goppelsroeder, *Z. anal. Ch.*, **7**, 195 (1868); Löwe, *Ibid.*, **14**, 117 (1875); Schantl, *Mikrochemie*, **2**, 174 (1924).

[2] Gutzeit, *Helv. Ch. Acta*, **12**, 713–40 (1929), *C.A.* **23**, 4644–5, has described some tests for Al involving organic reagents. Cf. Eegriwe, *Z. anal. Ch.*, **76**, 438–43 (1929), *C.A.* **23**, 2901.

[3] Sidener and Pettijohn, *Ind. Eng. Ch.*, **8**, 714 (1916); Blum, *J. Am. Ch. Soc.*, **38**, 1282 (1916).

[4] An indirect method involving precipitation of the Al by 8-hydroxyquinoline followed by titration of the precipitate with bromate has been suggested. Cf. Hillebrand and Lundell, p. 116.

[5] Cf. Goldschmidt's "thermite" process.

[6] Huttig and Brodkorb, *Z. anorg. allgem. Ch.*, **144**, 341 (1925).

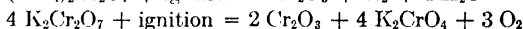
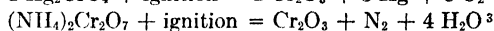
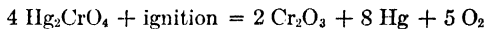
[7] v. Vegesack, *Ibid.*, **154**, 40 (1926); Smithells and Williams, *Nature*, **124**, 617–8 (1929), *C.A.* **24**, 1006, state that the melting point of Cr is nearer 1920° than 1500° as commonly given.

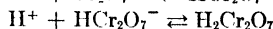
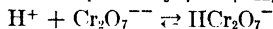
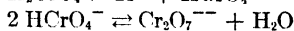
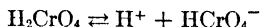
proof, (the "stainless" steels contain 8%–14% Cr), (3) a protective coating for less resistant metals. Some iron alloys containing as much as 30% Cr, others containing approximately 8% Ni and 18% Cr are gradually coming into more extensive use. The former are so hard that they cannot be machined. "Nichrome" wire (Ni 80%, Cr 20%) is extensively used for heating electrically.

2. Occurrence. — Chromium is not found native. Chromite, Cr_2O_3FeO, is the chief ore. It is fairly widely distributed, but commercially is obtainable principally from southern Rhodesia and British India; in fact, the British Empire controls well over 60% of the world's production, which, in 1928, amounted to somewhat less than 400,000 metric tons of ore, averaging 35%–55% Cr_2O_3. Metallic chromium is not in great demand commercially. It sells for $2–$5 per pound, depending upon the form, i.e., bar, powder, etc., and purity.

3. Preparation. — The major portion of all chromite mined is converted into ferrochrome and chromium salts. Some is also used as a refractory material for lining furnaces. Fusion of chromite with Na_2CO_3 produces Na_2CrO_4, which may be removed by leaching. Conversion to dichromate, followed by electrolysis, yields the metal. It may also be obtained (1) by heating Cr_2O_3 with carbon;[1] (2) by the "thermite" process, i.e., ignition of the oxide with Al; (3) by fusing $CrCl_3$ with Zn, Cd, or Mg, using KCl and NaCl as a flux and removing the excess of the Zn, Cd, or Mg by treatment with HNO_3, which does not dissolve Cr°.[2]

4. Oxides and Hydroxides. — Chromous oxide has not been isolated. The corresponding hydroxide, $Cr(OH)_2$, brownish, is made by treating $CrCl_2$ with NaOH. Chromic oxide, Cr_2O_3, green, is made by a great variety of methods, among which are the following:

$$4\,Hg_2CrO_4 + \text{ignition} = 2\,Cr_2O_3 + 8\,Hg + 5\,O_2$$
$$(NH_4)_2Cr_2O_7 + \text{ignition} = Cr_2O_3 + N_2 + 4\,H_2O$$ [3]
$$4\,K_2Cr_2O_7 + \text{ignition} = 2\,Cr_2O_3 + 4\,K_2CrO_4 + 3\,O_2$$

Chromic oxide may be easily fused in the electric furnace. Powerful reducing agents convert it to the metal (cf. 3). Ignited above 500° the oxide becomes comparatively insoluble in acids. Chromic hydroxide, $Cr(OH)_3$,[4] gray green, is precipitated by adding a base to chromic solutions. That formed by precipitating with fixed alkalis retains traces of the alkali not easily removed by washing. Chromic anhydride,[5] CrO_3, is formed as brown-red needles upon addition of concentrated H_2SO_4 to a concentrated solution of $Cr_2O_7^{--}$. To be freed from H_2SO_4 it must be recrystallized from water, in which it is readily soluble, or treated with the necessary amount of $BaCrO_4$. It is also prepared by transposition of $BaCrO_4$ with HNO_3 or H_2SO_4; $PbCrO_4$ with H_2SO_4; Ag_2CrO_4 with HCl, etc. It decomposes at about 190° into Cr_2O_3 and O_2. It is used as a mordant in dyeing silk and wool, but not cotton. It is a powerful oxidizing agent, being itself reduced to Cr^{+3}. Treated with water, CrO_3 is believed by some workers to yield H_2CrO_4; by others, $H_2Cr_2O_7$.[6] A third viewpoint involves the equilibria:

$$H_2CrO_4 \rightleftarrows H^+ + HCrO_4^-$$
$$2\,HCrO_4^- \rightleftarrows Cr_2O_7^{--} + H_2O$$
$$H^+ + Cr_2O_7^{--} \rightleftarrows HCr_2O_7^-$$
$$H^+ + HCr_2O_7^- \rightleftarrows H_2Cr_2O_7$$

[1] Cf. Rohn, *Z. Metallk.*, **16**, 275 (1924).

[2] Gaylor, *Metallwirtschaft*, **9**, 677–9 (1930), *C.A.* **24**, 5595, discusses the preparation and properties of chemically pure Cr.

[3] Hooton, *J. Ch. Soc.* (*Proc.*), **24**, 27 (1908), found that heating under different conditions apparently gives different products. Cf. Henrich, *Ch. Ztg.*, **35**, 864 (1911).

[4] Cf. Weiser, *J. Phys. Ch.*, **26**, 401 (1922); **24**, 277 (1920); Bjerrum, *Z. physik. Ch.*, **73**, 724 (1910).

[5] For other oxides, see: Simon and Schmidt, *Z. anorg. allgem. Ch.*, **153**, 191–218 (1926).

[6] Abegg, IV, 1, Pt. 2, 306; Auerbach, *Z. anorg. allgem. Ch.*, **126**, 54 (1923); Sabalitschka and Kubisch, *Pharm. Zentralhalle*, **65**, 272–4 (1924); Carriere and Castel, *Compt. rend.*, **187**, 1292–4 (1928).

Two series of salts are formed: chromates, M_2CrO_4, and dichromates, $M_2Cr_2O_7$. The former are yellow, the latter orange, unless the positive ion is colored. Chromates are found in neutral or alkaline solution, dichromates in acid solution.

5. Solubilities. — *a. Metal.* — Chromium is soluble in HCl, yielding blue $CrCl_2$ if the air is excluded, otherwise $CrCl_3$. Chlorine or bromine attack it with formation of the corresponding tervalent halide. Dilute H_2SO_4 forms $Cr_2(SO_4)_3$ or $CrSO_4$ (see above); concentrated H_2SO_4, like HNO_3, dilute or concentrated, tends to induce passivity. Chromium is not affected by water or moist air at 100°; but heated above 200° it is oxidized to Cr_2O_3, rapidly in presence of NaOH.

b. Oxides and Hydroxides. — Chromic oxide, Cr_2O_3, is insoluble in H_2O, slowly soluble in acids,[1] best in HCl, but not if previously ignited (cf. 4). The hydroxide is insoluble in H_2O, soluble in acids, sparingly soluble in NH_4OH to form a red complex,[2] soluble in the fixed alkalis, forming green chromite,[3] (CrO_3^{-3} or CrO_2^-);[4] reprecipitated upon standing or boiling. Further addition of alkali has little effect. The presence of other metallic hydroxides, e.g., $Fe(OH)_3$, etc., hinders the solution in fixed alkalis. Chromic anhydride, CrO_3, is very soluble in H_2O; it is also soluble in reducing acids, forming Cr^{+3}.

c. Salts. — Chromic sulfide is not formed in the wet way, being decomposed by water; the phosphate is insoluble in water. The chloride exists in two[5] modifications; a green, deliquescent, soluble chloride, and a violet, sublimed, chromic chloride, anhydrous and insoluble in water or in dilute or concentrated acids. The presence of a very small amount of $CrCl_2$ or $SnCl_2$ at once renders this modification soluble in water. The bromide and sulfate also exist in soluble and insoluble modifications; the nitrate and basic nitrates are readily soluble in water. There are many double salts, the sulfates[6] of Cr and the alkali metals forming alums similar to the corresponding Al compounds. Complexes are also formed with many other substances, e.g., HCN, H_2SO_4, NH_3, organic compounds containing OH^-, $C_2H_3O_2^-$, etc. These complexes differ in reaction from Cr^{+3}; also, in many cases, only a portion of the normally negative ion can be precipitated, e.g., from $CrCl_3$ only one- or two-thirds, from the sulfate only one- or two-thirds, etc. In either of these cases, addition of acetate tends to release the balance of the desired ion.[7] There are two modifications of solutions of chromic salts, one having a green color and the other violet to red. All normal chromic salts in solution have an acid reaction, being partially hydrolyzed.

6. Reactions. [8] — *a.* Alkali hydroxides[9] and carbonates precipitate from solutions of Cr^{+3}, chromic hydroxide[10] (see §124, 6, *a*), $Cr(OH)_3$, gray green

[1] Mumford and Gilbert, *J. Ch. Soc.* (*Trans.*), **123**, 471 (1923).

[2] Cf. Jowitschitsch, *Monatsh.*, **34**, 225–42 (1913).

[3] Cf. Müller, *Z. angew. Ch.*, **35**, 557–8 (1922).

[4] Probably a colloidal effect of peptization of the $Cr(OH)_3$ by OH^-.

[5] Bjerrum, *Z. physik. Ch.*, **73**, 724 (1910); **59**, 581 (1907), claims three: a dark green, a light green, and a violet. Cf. Demassieux and Heyrovsky, *J. ch. phys.*, **26**, 219–23 (1929), *C.A.* **23**, 5124.

[6] Krauss, *et al.*, *Z. anorg. allgem. Ch.*, **179**, 413–7 (1929), *C.A.* **23**, 2673.

[7] Willard and Schneidewind, *Trans. Am. Electroch. Soc.*, **56**, 333–49 (1929).

[8] Chromous salts are rapidly oxidized on exposure to the air, hence are seldom encountered in analysis.

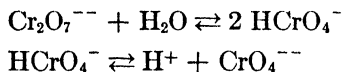
[9] Cf. Britton, *J. Ch. Soc.*, **127**, 2127 (1925).

[10] Chromic hydroxide is not precipitated in the presence of tartrates or glycerol.

to gray blue, insoluble in water, soluble in acids and excess of the fixed alkalis, the latter yielding chromites, e.g., $Cr(OH)_3 + NaOH = NaCrO_2 + 2\ H_2O$;[1] $Cr(OH)_3$ is completely reprecipitated on long boiling (distinction from Al), or on heating with an excess of NH_4Cl (see: §124, 6, *a*). The presence of $Fe(OH)_3$ and some other compounds greatly hinders the solution in fixed alkalis, hence chromium cannot be separated from iron by excess of fixed alkali. Chromium hydroxide is slightly soluble in excess of cold NH_4OH to give a violet solution (cf. 5, *b*). The hydroxide is completely, though slowly, reprecipitated on boiling. The precipitate formed with alkali carbonates is practically free from carbonate: $2\ CrCl_3 + 3\ Na_2CO_3 + 3\ H_2O = 2\ Cr(OH)_3 + 6\ NaCl + 3\ CO_2$. Barium carbonate precipitates chromium from its solutions (better from $CrCl_3$) as a hydroxide with some basic salt, the precipitation being complete after long digestion in the cold (separation from Group IV).

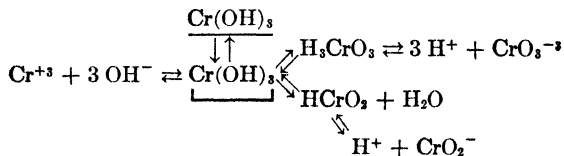
Dichromates are changed to normal chromates by alkali hydroxides or carbonates. The reaction is simply one of neutralization:

$$Cr_2O_7^{--} + H_2O \rightleftarrows 2\ HCrO_4^-$$

$$HCrO_4^- \rightleftarrows H^+ + CrO_4^{--}$$

b. Chromium forms no basic acetate and remains in solution when the corresponding compounds of Al and Fe are precipitated. Excess of Fe, however, may bring about fairly complete precipitation of Cr, due probably to adsorption. Potassium cyanide precipitates $Cr(OH)_3$. Oxalates and ferrocyanides cause no precipitation. Chromic acid, H_2CrO_4, is reduced to Cr^{+3} by $K_4Fe(CN)_6$ and CNS^-.

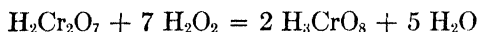
c. Nitrites or nitrates are without action upon Cr^{+3}, but fusion of Cr^{+3} salts with nitrite or nitrate and alkali carbonate yields a chromate, soluble in water (separation from Fe and Al). The action of H_2O_2 on ions of chromium depends on several factors, e.g., initial state of oxidation, acidity (or alkalinity) of the system, temperature, amount of H_2O_2 present, etc. Heating chromite ion with H_2O_2 gives chromate: $2\ NaCrO_2 + 3\ H_2O_2 + 2\ NaOH = 2\ Na_2CrO_4 + 4\ H_2O$. In acid solution, Cr^{+3} is unaffected.

[1] It should be noted that the system is probably distinctly more complex than indicated above:

$$\begin{array}{ccccl} & & \underline{Cr(OH)_3} & & \\ & & \downarrow\uparrow & \nearrow\swarrow & H_3CrO_3 \rightleftarrows 3\ H^+ + CrO_3^{-3} \\ Cr^{+3} + 3\ OH^- & \rightleftarrows & Cr(OH)_3 & & \\ & & \sqcup & \searrow\nwarrow & HCrO_2 + H_2O \\ & & & & \quad \updownarrow \\ & & & & \quad H^+ + CrO_2^- \end{array}$$

The addition of a base furnishing sufficient OH^- will, of course, yield both CrO_3^{-3} and CrO_2^-, the amount of each depending upon conditions. The colloid chemist looks upon this entire phenomenon as one of peptization. [Cf. Nagel, *J. Phys. Ch.*, **19**, 331, 569 (1915).]

With the higher valence of chromium, a number of products may be obtained, concerning some of which there is considerable uncertainty as to the composition.[1] If a cold, alkaline chromate is treated with H_2O_2, a red solution (R_3CrO_8) is obtained. If the original solution is neutral instead of alkaline, the color developed is purple (RH_2CrO_7 or $RCrO_5$?). In both cases the color gradually disappears with return of the original color. Neither form can be extracted with ether. If a cold, acid solution of Cr^{+6} is treated with H_2O_2 a deep, indigo blue ($HCrO_5 - H_3CrO_7 - H_3CrO_8$) is obtained, more soluble in ether, amyl alcohol or ethyl acetate than in H_2O, hence readily extracted from aqueous solution by these solvents. The blue perchromic acid thus obtained is more stable below 0° than above, decomposing fairly rapidly at room temperature, to give Cr^{+3}:

$$H_2Cr_2O_7 + 7\ H_2O_2 = 2\ H_3CrO_8 + 5\ H_2O$$

$$2\ H_3CrO_8 + 3\ H_2SO_4 = Cr_2(SO_4)_3 + 6\ H_2O + 5\ O_2$$

According to Storer[2] the formation of the blue perchromic acid is an excellent test for $Cr_2O_7^{--}$, since one part in about 40,000 may be detected readily, especially if ether is used (see, however, §44).

d. Hypophosphorous acid reduces Cr^{+6} to Cr^{+3}. Soluble phosphates, as Na_2HPO_4, precipitate chromic phosphate, $CrPO_4$,[3] insoluble in acetic acid, decomposed by boiling with NaOH, leaving the phosphate in solution.

e. Hydrosulfic acid is without action upon acid or neutral solutions of Cr^{+3}; CrO_2^- is precipitated as $Cr(OH)_3$: $NaCrO_2 + H_2S + H_2O = Cr(OH)_3 + NaHS$. Chromates and dichromates are reduced to Cr^{+3} with liberation of sulfur; in neutral or alkaline solution $Cr(OH)_3$ is formed: $K_2Cr_2O_7 + 5\ H_2S = 2\ Cr(OH)_3 + 2\ KHS + 3\ S + H_2O$; in acid solution only sulfur is precipitated: $K_2Cr_2O_7 + 3\ H_2S + 8\ HCl = 2\ CrCl_3 + 2\ KCl + 3\ S + 7\ H_2O$. Alkali sulfides precipitate Cr^{+3} as the hydroxide, liberating H_2S: $2\ CrCl_3 + 3\ (NH_4)_2S + 6\ H_2O = 2\ Cr(OH)_3 + 6\ NH_4Cl + 3\ H_2S$. Chromates and dichromates are reduced and yield a precipitate of $Cr(OH)_3$ and S:[4] $2\ Na_2CrO_4 + 7\ (NH_4)_2S = 2\ Cr(OH)_3 + 4\ NaHS + 3\ S + 2\ H_2O + 14\ NH_3$. Soluble sulfites and thiosulfates reduce Cr^{+6} in acid solution.[5]

f. Hydrochloric acid reduces Cr^{+6} to Cr^{+3} on boiling: $2\ Na_2CrO_4 + 16\ HCl = 2\ CrCl_3 + 4\ NaCl + 3\ Cl_2 + 8\ H_2O$; more readily without evolution of Cl_2 in presence of other easily oxidized agents, e.g., alcohol, oxalic acid, etc.: $K_2Cr_2O_7 + 8\ HCl + 3\ C_2H_5OH = 2\ KCl + 2\ CrCl_3 +$

[1] A good summary is to be found in Abegg's Handbuch, IV, 1, Pt. 2, p. 415–30 (1921).

[2] Storer, *Proc. Am. Acad. Sci.*, **4**, 338 (1859).

[3] Joseph and Rae, *J. Ch. Soc.*, **111**, 196 (1917).

[4] Dunnicliff and Soni, *J. Phys. Ch.*, **33**, 81–7 (1929), *C.A.* **23**, 1074, state that K_2CrO_4 and H_2S give $Cr(OH)_3$, K_2S, and $K_2S_2O_3$.

[5] Donath, *J. Ch. Soc.*, **36**, 401 (1879); Longi, *Gazz. ch. ital.*, **26**, II, 119 (1896), for sulfites see: Recoura, *Ann. ch. phys.*, [7] **4**, 494 (1895); Colson, *Ibid.*, [8] **12**, 433–67 (1907).

3 CH_3CHO (acetaldehyde) + 7 H_2O. If a dry chromate or dichromate is heated with H_2SO_4 and a chloride (transposable by H_2SO_4), brown fumes of chromyl chloride (chromium dioxydichloride or chlorochromic acid) are evolved: $K_2Cr_2O_7 + 4\ NaCl + 3\ H_2SO_4 = 2\ CrO_2Cl_2 + K_2SO_4 + 2\ Na_2SO_4 + 3\ H_2O$.[1] Hydrobromic acid reduces Cr^{+6} to Cr^{+3} with evolution of Br_2; hydriodic acid also causes reduction. In the presence of HCl or H_2SO_4, all of the bromine or iodine is set free:

$$K_2Cr_2O_7 + 6\ HI + 4\ H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 3\ I_2 + 7\ H_2O$$

Hydriodic acid acts most readily upon Cr^{+6}, hydrochloric least readily. Chromic hydroxide and chromic salts, when boiled with chloric or bromic acid, or ClO_3^- or BrO_3^-, yield $Cr_2O_7^{--}$.

g. Soluble arsenites and arsenates form corresponding salts with Cr^{+3}. Dichromates are instantly reduced to Cr^{+3} by AsO_3^{-3}. Chromic acid boiled with arsenious acid in excess gives chromic arsenate, $CrAsO_4$.[2]

h. Dichromates color an acid solution of chromic salts brown yellow; on addition of NH_4OH, a precipitate of the same color is obtained, chromic chromate.[3] The alkali metals form two classes of salts with Cr^{+6}, yellow chromates, and orange dichromates. The chromates of the alkalis, and those of Mg, Ca, Zn and Cu are soluble; those of Sr and Hg^{++} [4] are slightly soluble; those of Ba, Mn,[5] Bi,[6] Hg_2^{++}, Ag and Pb are insoluble. Alkali chromates or dichromates yield precipitates of the normal chromate (under certain conditions, the dichromate) when treated with Ag^+, Pb^{++}, Hg_2^{++} or Ba^{++}.[7] Silver chromate, Ag_2CrO_4, is dark reddish brown, soluble in HNO_3 and NH_4OH; lead chromate, $PbCrO_4$, is yellow, soluble in 3 *N* HNO_3, insoluble in acetic acid; barium chromate, $BaCrO_4$, yellow, is soluble in HCl, HNO_3, and slightly soluble even in chromic acid.[8]

7. Ignition. — Chromic oxide, chromic salts, and chromates dissolve in beads of microcosmic salt, and of borax, before the blowpipe, in both reducing and oxidizing flames, with a yellowish-green tint while hot, becoming emerald green when cold. When ignited on charcoal, the carbon reduces Cr^{+6}, and a green mass, Cr_2O_3, is left (cf. 3). Fusion of chromium compounds with an alkali carbonate and a nitrite, nitrate, chlorate, bromate, or iodate results in formation of an alkali chromate, soluble in water (distinction from Al and Fe).

[1] Thompson, *Phil. Trans. Roy. Soc.*, **117**, 159 (1827); Thorpe, *J. Ch. Soc.*, **21**, 514 (1868); cf. Friend, VII, Pt. 3, p. 28.
[2] Neville, *J. Ch. Soc.*, **31**, 283 (1877).
[3] Maus, *Pogg. Ann.*, **9**, 127 (1827); Manchot and Kraus, *Ber.*, **39**, 3512 (1906).
[4] Cox, *Z. anorg. allgem. Ch.*, **40**, 146 (1904); **50**, 226 (1906).
[5] Cf. Friend, VII, Pt. 3, p. 57.
[6] The neutral salt has not been prepared, bismuthyl dichromate, $(BiO)_2Cr_2O_7$, is often obtained; cf. Friend, VII, Pt. 3, p. 48.
[7] Rüdisüle, V, 954.
[8] Cf. Waddell, *Analyst*, **43**, 287 (1918).

8. Detection. — *a.* If present as chromate or dichromate, Cr is reduced by HCl + CH_2O (formaldehyde), before adjustment of acidity for the precipitation of Group II. The Cr^{+3} is precipitated in Group III along with Fe^{+3} and Al^{+3} by NH_4OH in the presence of NH_4Cl. Boiling with NaOH and H_2O_2 oxidizes the chromium to CrO_4^{--}, leaving the iron as $Fe(OH)_3$ and the aluminum as AlO_2^-. Filtration removes the iron; boiling with NH_4Cl (the sulfate is better) precipitates $Al(OH)_3$ and aids in removal of excess peroxide. The Cr is identified in the filtrate (a) after acidulation with acetic acid by the formation of yellow lead chromate; (b) after acidification with H_2SO_4 by the formation of a vanishing blue color (H_3CrO_8) upon addition of H_2O_2 (cf. 6, *c*).[1]

b. A number of organic reagents have been suggested for the detection of chromium, practically all of which depend upon their reaction with chromate or dichromate. A trace of α-naphthylamine added to a solution of Cr^{+6} gives, on addition of tartaric acid, a deep blue color; benzidine and diphenylamine also produce a blue color, pyrogallol dimethyl ether forms a yellow color; diphenylcarbazide produces a violet tint.[2]

9. Determination. — Chromium may be determined *gravimetrically* (a) by precipitation as the hydroxide and ignition to the oxide in a reducing atmosphere; (b) by precipitation and weighing as $PbCrO_4$ (or $BaCrO_4$). Neither method finds extensive application. *Volumetrically,* chromium is first oxidized to Cr^{+6} and then titrated with some reducing agent such as (a) $FeSO_4$ in excess, the latter being determined by back titration with standardized $K_2Cr_2O_7$ or $KMnO_4$, the end point being determined electrometrically[3] or in case of $Cr_2O_7^{--}$, by using diphenylamine[4] or diphenylcarbazide as an internal indicator; (b) KI in excess, the liberated I_2 being determined with $Na_2S_2O_3$. (Fe^{+3} may interfere.)

10. Oxidation and Reduction. — Chromous compounds are very strong reducing agents, changing Hg^{++} to Hg°, Cu^{++} to Cu°, Sn^{++} to Sn°, etc. Chromic compounds are oxidized to CrO_4^{--} by ClO_3^-, alkali peroxide, MnO_4^-,[5] MnO_2 and PbO_2[6] in acid solution; in alkali mixture by Na_2O_2, ClO^-, BrO^-, PbO_2, Ag_2O,[7] Hg_2O, HgO, CuO, MnO_4^-, MnO_4^{--}, etc. A chromate is also formed when Cr^{+3} compounds are fused with an alkali carbonate and an oxidizing agent (cf. 7). Chromic oxide (not ignited) or $CrCl_3$ heated in a current of chlorine, become CrO_2Cl_2.[8] Chromates and

[1] Barreswill, *Ann. ch. phys.*, [3] **20**, 364 (1847); cf. Lutz and Jacoby, *Latvijas Augstskolas Raksti*, **3**, 109–37 (1922), *C.A.* **17**, 3147.

[2] van Eck, *Ch. Weekblad*, **12**, 6–8 (1915); Stover, *J. Am. Ch. Soc.*, **50**, 2363 (1928); Evans, *Analyst*, **46**, 285 (1921). Cf. Gutzeit, *Helv. Ch. Acta*, **12**, 713–40 (1929), *C.A.* **23**, 4644, who describes a number of characteristic tests.

[3] Cf. Britton, *J. Ch. Soc.*, **125**, 1572–82 (1924); Hostetter and Roberts, *J. Am. Ch. Soc.*, **41**, 1337 (1919).

[4] Cf. Kolthoff, *J. Am. Ch. Soc.*, **53**, 2902 (1931).

[5] Fales and Roller, *J. Am. Ch. Soc.*, **51**, 345 (1929).

[6] Terni, *Gazz. ch. ital.*, **43**, II, 63–5 (1913).

[7] Hans, *Z. anorg. allgem. Ch.*, **140**, 337–8 (1924).

[8] Moissan, *Bull. soc. ch.*, [2] **34**, 70 (1880).

dichromates are reduced to Cr^{+3} by oxalate, ferrocyanide, thiocyanate, sulfide, thiosulfate, SO_2, H_2O_2 (in acid solution), etc. Of most common occurrence in qualitative analysis is the action of H_2S or alkali sulfides, resulting in the formation chiefly of sulfur, though some SO_3^{--} and SO_4^{--} are also obtained:[1] $K_2Cr_2O_7 + 8\ HCl + 3\ H_2S = 2\ CrCl_3 + 2\ KCl + 3\ S + 7\ H_2O$. The reactions with peroxide indicate the influence of conditions: (a) solution acid and cold — $K_2Cr_2O_7 + 7\ H_2O_2 + H_2SO_4 = 2\ H_3CrO_8 + K_2SO_4 + 5\ H_2O$; (b) solution acid and warm — $K_2Cr_2O_7 + 3\ H_2O_2 + 4\ H_2SO_4 = Cr_2(SO_4)_3 + K_2SO_4 + 7\ H_2O + 3\ O_2$; (c) solution alkaline — $2\ CrCl_3 + 10\ NaOH + 3\ H_2O_2 = 2\ Na_2CrO_4 + 6\ NaCl + 8\ H_2O$.

§126. Iron (Anglo-Saxon, *isen*) (Ferrum). Fe = 55.84. Atomic No. 26. Valence 2 and 3. Discovery prehistoric.

1. Physical Properties. — Density, 7.93 ± 0.03;[2] melting point, 1533° ± 1°;[3] boiling point, 2450° ± 50° at 36 mm. pressure.[4] Pure iron is silvery white, capable of taking a remarkably fine polish; it is among the most ductile of metals; it is the hardest of the ductile metals and in tenacity is surpassed only by cobalt and nickel. These properties are greatly influenced by the amount of impurity present, especially carbon. Iron softens at a red heat and may be welded at a white heat. Finely divided iron burns in the air when ignited; that made by reduction in hydrogen may ignite spontaneously when exposed to the air. Wrought iron contains less than 0.2% carbon, steel from 0.3% to 1.5%, and cast iron from 1.7% to 4.6%. Pure iron is attracted by the magnet, but does not retain its magnetism. High grade permanent magnets are made of silicon steel. Generally speaking, carbon steel is iron, containing — in addition to carbon — silicon, sulfur, phosphorus and manganese. Alloy steels contain in addition to the elements just mentioned, Ni, Cr, V, W, Mo, etc., either alone or combined, e.g., Cr-Ni, Cr-V, Cr-V-W, etc. The amount of the alloying agent varies considerably depending upon the properties desired, e.g., Cr may vary from less than 1% up to about 15%. Vanadium and molybdenum seldom run over a fraction of 1%, nickel as high as 8%, and tungsten up to 18%.

2. Occurrence. — Native iron is rarely found except in meteorites. The chief ores of iron are hematite, Fe_2O_3, red; brown hematite, $Fe_2O_3 \cdot nH_2O$; limonite, $2Fe_2O_3 \cdot 3H_2O$; magnetite, Fe_3O_4; and siderite, $FeCO_3$, often called spathic iron or kidney ore. Iron is found in practically all igneous rocks, most minerals, and is fourth in abundance in the earth's crust (outer 10 miles), the amount being slightly over 5%.[5] In the United States about 85% of the ore mined comes from the Lake Superior district, i.e., Minnesota and Michigan; three other states, — Alabama, Wisconsin and Pennsylvania — produce an additional 12%; the total averaging somewhat over 60 million tons per year, valued at approximately $4.00 per ton. The price varies, of course, with the quality of the ore, the basis being a guaranteed content of at least 51.50% iron, calculated as the metal. Pig iron sells for about $18 per ton; steel $40 and up, depending upon the kind and quality.[6]

3. Preparation. — Pure iron is not usually found in the market. It may be made by electrolysis and by heating its purified salts in hydrogen. The commercial metallurgy of iron involves the heating of a mixture of iron ore, coke and limestone to a high temper-

[1] Cf. Dunnicliff and Soni, *J. Phys. Ch.*, **33**, 81–7 (1929).
[2] Davey, *Phys. Rev.*, [2] **25**, 753 (1925).
[3] Burgess and Waltenberg, *Z. anorg. allgem. Ch.*, **82**, 361 (1913).
[4] Ruff and Bormann, *Ibid.*, **88**, 405 (1914).
[5] U. S. Geol. Survey, Prof. Paper 127, p. 20.
[6] Mineral Ind., **1928**, p. 298 *et seq.*

ature in a blast furnace. Under the reducing conditions encountered, metallic iron is formed which gathers in the liquid state at the bottom of the furnace, from which it may be removed and cast into pigs or immediately started through a refining process, e.g., open hearth, Bessemer, etc.

4. Oxides and Hydroxides. — Ferrous oxide, FeO, black, is obtained (1) by passing steam over Fe at 570° or above: $Fe + H_2O = FeO + H_2$; (2) by reduction of Fe_2O_3 at 300° in an atmosphere of hydrogen; (3) by heating $FeC_2O_4 \cdot 2H_2O$ to 160°, air being excluded.[1]

Ferrous hydroxide, $Fe(OH)_2$, is formed upon treating the solution of a ferrous salt with excess OH^-; it is white when pure, but usually green from partial oxidation. Ferric oxide, Fe_2O_3, is formed by heating FeO, $Fe(OH)_2$, or any ferrous salt of a volatile or organic acid in the air; more rapidly by heating $Fe(OH)_3$, $Fe(NO_3)_3$, or $Fe_2(SO_4)_3$. Ferric hydroxide, $Fe_2O_3 \cdot nH_2O$,[2] red brown, is obtained upon treating the solution of a ferric salt with excess OH^- or alkali carbonate. Precipitation from a cold solution often gives a positively charged colloid which may coagulate upon boiling or treating with a bi- or tervalent anion. Magnetic iron oxide, magnetite, Fe_3O_4, is slowly formed by heating FeO or Fe_2O_3; by passing steam over Fe heated below 570°: $3\ Fe + 4\ H_2O = Fe_3O_4 + 4\ H_2$.[3] It is believed that magnetite is not a mechanical mixture of FeO and Fe_2O_3, but that it is ferrous ferrite, $FeFe_2O_4$ [or $Fe(FeO_2)_2$]. Other ferrites have been prepared, e.g., $CaFe_2O_4$, $BaFe_2O_4$, $MgFe_2O_4$, $ZnFe_2O_4$, etc., by fusing Fe_2O_3 with the appropriate basic oxide. Treatment of sodium ferrite with water gives ferrous acid, $HFeO_2$. Some ferrates have been obtained by heating a mixture of the hydroxide and ferric hydroxide in oxygen, e.g., $BaFeO_3$. Inclusion of a strong oxidizing agent yields the perferrate. Sodium perferrate, Na_2FeO_4, is made (a) by electrolysis; (b) heating iron filings, FeO or Fe_2O_3 to a red heat with $NaNO_3$; (c) by heating $Fe(OH)_3$ with Na_2O_2; (d) by treating a suspension of $Fe(OH)_3$ in NaOH with Cl_2 or Br_2, the temperature being below 50°. The product slowly decomposes upon standing: $4\ Na_2FeO_4 + 10\ H_2O = 4\ Fe(OH)_3 + 8\ NaOH + 3\ O_2$. Addition of a barium salt precipitates the comparatively stable barium perferrate. This compound is slightly soluble and not decomposed by H_2O or cold, dilute H_2SO_4.

5. Solubilities. — *a. Metal.* — Iron dissolves in HCl and dilute H_2SO_4, forming Fe^{++}, with liberation of H_2 (Eq. 1); concentrated, cold H_2SO_4 has no action, but if hot, SO_2 is evolved and Fe^{+3} formed (Eq. 2); in moderately dilute HNO_3, with heat, Fe^{+3} and NO are the chief products (Eq. 3); in cold, dilute HNO_3, Fe^{++} and NH_4^+ (Eq. 4), or N_2O (Eq. 5), or H_2 (Eq. 6),[4] result. Cold concentrated HNO_3 and other strong oxidizing agents, e.g., chromic acid, induce passivity, which may be destroyed by immersion in reducing agents or scratching the surface of the metal.

(1) $Fe + H_2SO_4 = FeSO_4 + H_2$

(2) $2\ Fe + 6\ H_2SO_4 = Fe_2(SO_4)_3 + 3\ SO_2 + 6\ H_2O$

(3) $Fe + 4\ HNO_3 = Fe(NO_3)_3 + NO + 2\ H_2O$

(4) $4\ Fe + 10\ HNO_3 = 4\ Fe(NO_3)_2 + NH_4NO_3 + 3\ H_2O$

(5) $4\ Fe + 10\ HNO_3 = 4\ Fe(NO_3)_2 + N_2O + 5\ H_2O$

(6) $Fe + 2\ HNO_3 = Fe(NO_3)_2 + H_2$

When dissolving the iron of commerce in HCl, the carbon that it always contains as carbide, Fe_3C, will pass off as gaseous hydrocarbons,[5] and the uncombined or graphitic carbon will remain undissolved. Iron is attacked by moist air, forming chiefly a hydrated oxide, $2Fe_2O_3 \cdot 3H_2O$, iron rust.

b. Oxides and Hydroxides. — Ferrous oxide and hydroxide unite with acids, forming ferrous salts, usually mixed with more or less Fe^{+3}. The ferrous salts are perhaps more

[1] Vogel, *J. prakt. Ch.*, **63**, 187 (1854) states that pyrophoric iron is obtained.
[2] Usually written $Fe(OH)_3$, but see: Gmelin, 8th ed., No. 59, Pt. B, p. 122.
[3] Gmelin, *loc. cit.*, p. 38.
[4] Langlois, *Ann. ch. phys.*, [3] **48**, 502 (1856).
[5] Campbell, *Am. Ch. J.*, **18**, 836 (1896).

readily prepared by the action of dilute acids upon the metal, or upon $FeCO_3$ or FeS. Ferric oxide dissolves in acids, quite slowly if it has been ignited. Hydrochloric acid is the best solvent; warm H_2SO_4 (8 : 3) has also been recommended. If the oxide is heated with alkalis or alkali carbonates, it then dissolves more readily in acids. $NaFeO_2$ on treatment with water gives ferrous acid, $HFeO_2$ (cf. 4). Ferric hydroxide is insoluble in water, readily soluble in acids. Freshly precipitated $Fe(OH)_3$ readily dissolves in $FeCl_3$ and in $CrCl_3$, not in $AlCl_3$.[1] A solution of $Fe(OH)_3$ in $FeCl_3$ forms a residue on evaporation to dryness which will redissolve in water if not more than 10 parts of Fe_2O_3 are present to one of $FeCl_3$. Ferrous ferrite, Fe_3O_4, treated with an insufficient amount of HCl, forms $FeCl_2$ and Fe_2O_3; treated with excess HCl, a mixture of $FeCl_2$ and $FeCl_3$ is obtained, which, when treated with excess NH_4OH and dried at 100°, again exhibits the magnetic properties of the original.

c. Salts. — Ferrous salts, in crystals and in solution, have a pale green color. Solutions of the salts have a slight acid reaction to litmus. The sulfate, $FeSO_4 \cdot 7H_2O$, is efflorescent; the halides are deliquescent. Solutions of Fe^{++} are unstable in contact with air, tending to change to Fe^{+3}, which forms a basic salt, more or less insoluble in H_2O. Ferric salts in solution have a brownish-yellow color,[2] redden litmus and color the skin yellow. The chloride, bromide, nitrate and sulfate are deliquescent. The sulfate is soluble in alcohol (separation from $FeSO_4$). Ferric chloride is soluble in ether saturated with HCl (separation from Al). Solutions of Fe^{+3}, when boiled, frequently precipitate a large portion of the iron as basic salt, especially if other soluble salts are present. Among the ferrous salts, the arsenate, carbonate, ferricyanide, hydroxide, oxalate and phosphate are insoluble. Among the ferric salts, the arsenate, ferrocyanide, hydroxide and phosphate are insoluble. Solubility figures for many of these salts are very discordant.[3]

6. **Reactions.** — *a.* The alkali hydroxides precipitate ferrous hydroxide, $Fe(OH)_2$, white if pure, but seldom obtained sufficiently free from $Fe(OH)_3$ to be white. It quickly changes, in the air, to ferroferrichydroxide,[4] of a dirty green to black color, then to $Fe(OH)_3$, reddish brown. The fixed alkalis are adsorbed by $Fe(OH)_2$. Ammonium salts, sugar, and many organic acids, to a slight extent, dissolve $Fe(OH)_2$ or prevent its formation. Soluble carbonates precipitate from Fe^{++} solutions, ferrous carbonate, $FeCO_3$, white if pure, but soon changing in the air to $Fe(OH)_3$.

Solutions of Fe^{+3} when treated with the alkali hydroxides, or carbonates, yield ferric hydroxide, $Fe(OH)_3$ ($Fe_2O_3 \cdot 3H_2O$), reddish brown, insoluble in excess of reagent[5] (distinction from Al and Cr, which are soluble in excess of the fixed alkali hydroxides, and from Co, Ni and Zn, which are

[1] An explanation of this curious situation has not been found in the literature.

[2] $FePO_4$ is colorless and the color of $Fe_2(SO_4)_3$ depends upon the concentration.

[3] Latimer and Hildebrand, p. 389, give 2×10^{-14} for the solubility product of $Fe(OH)_2$; Britton, p. 256, gives 4.5×10^{-21}.

[4] Sandonnini, *Gazz. ch. ital.*, **60**, 321–36 (1930), *C.A.* **24**, 3962, has studied the oxidation of $Fe(OH)_2$.

[5] $Fe(OH)_3$ is soluble in excess KOH in presence of ozone. Oxidation is probably involved.

soluble in NH_4OH). Salts of the fixed alkalis are adsorbed by this precipitate and held with great tenacity, also the precipitate obtained by addition of the fixed alkali carbonates invariably contains traces of a carbonate. Freshly precipitated $BaCO_3$ completely precipitates Fe^{+3} in the cold as $Fe(OH)_3$ (separation of Fe^{+3}, Al^{+3} and Cr^{+3} from Fe^{++}, Co^{++}, Ni^{++}, Mn^{++} and Zn^{++}): $2\ FeCl_3 + 3\ BaCO_3 + 3\ H_2O = 2\ Fe(OH)_3 + 3\ BaCl_2 + 3\ CO_2$. The mixture should be allowed to stand several hours (Cr^{+3} precipitates more slowly than Al^{+3} or Fe^{+3}), and SO_4^{--} must be absent, because freshly precipitated $BaCO_3$ reacts with solutions of the fourth group sulfates, e.g., $NiSO_4 + BaCO_3 = BaSO_4 + NiCO_3$. The reaction takes place most readily if the metals are present as chlorides. If the precipitate obtained is treated with an excess of dilute H_2SO_4, the $Fe(OH)_3$ dissolves, the Ba^{++} and excess of $BaCO_3$ being converted to the insoluble sulfate. Freshly precipitated carbonates of Ca, Mg, Mn, Zn and Cu react like $BaCO_3$.[1]

b. Oxalic acid and soluble oxalates precipitate from solutions of Fe^{++}, ferrous oxalate, FeC_2O_4, yellowish white, crystalline, insoluble in H_2O, soluble in HCl, HNO_3 and H_2SO_4; Fe^{+3} is not precipitated by oxalates, except as reduction to Fe^{++} takes place.

The acetates, e.g., $NaC_2H_3O_2$, used in large excess, form with Fe^{+3},[2] a dull red solution of a complex basic acetate,[3] $Fe_3\left[\begin{matrix}(C_2H_3O_2)_6\\(OH)_2\end{matrix}\right]C_2H_3O_2$, which upon standing, or more quickly with boiling, precipitates as an oxyacetate, $Fe_3(C_2H_3O_2)(OH)_2O_3$. The reaction goes to completion at the boiling point, but tends to reverse upon cooling, especially if a large amount of iron is present.[4] This is used as a separation of Fe^{+3} and Al^{+3} (Cr^{+3} and PO_4^{-3})[5] from the fourth group metals. The red color of the ferric acetate solution is not affected by $HgCl_2$ (distinction from $Fe(CNS)_3$). The basic precipitate is soluble in HCl, HNO_3 and H_2SO_4, and transposed by alkali hydroxides to the hydroxide.

Potassium cyanide gives, with Fe^{++}, a yellowish-red precipitate of $Fe(CN)_2$,[6] which dissolves in excess of the reagent to form $Fe(CN)_6^{-4}$:

[1] ZnO is being used to a considerable extent, instead of $BaCO_3$, in the industrial laboratories.

[2] If the solution contains no excess of free acid.

[3] Weinland and Gussmann, *Z. anorg. allgem. Ch.*, **66**, 157 (1910).

[4] For complete precipitation, the solution of Fe^{+3} is neutralized with NH_4OH until a precipitate forms that does not disappear upon stirring. The solution is then cleared with a few drops of HCl (as little as necessary). After addition of 10–15 cc. of 3 *N* $NaC_2H_3O_2$ and dilution to 100 cc., the solution is boiled 3–5 minutes and then the flocculent precipitate is quickly removed by rapid filtration.

[5] PO_4^{-3}, if present, is precipitated as $FePO_4$ in the basic acetate precipitation; also, while Cr of itself will not give a basic acetate precipitate, it may be precipitated fairly completely if excess of Fe or Al is present. With excess Cr present, precipitation of Fe and Al is incomplete.

[6] Browning, *J. Ch. Soc.*, **77**, 1234 (1900), says that the isocyanide, $Fe(NC)_2$, is formed,

$Fe(CN)_2 + 4\ KCN = K_4Fe(CN)_6$. Solutions of Fe^{+3} yield with CN^-, a precipitate of ferric hydroxide with evolution of HCN (Eq. 1). A small amount of the $Fe(OH)_3$ is dissolved in excess CN^-, forming $Fe(CN)_6^{-3}$,[1] but the usual method of preparing ferricyanides is by oxidation of the ferrocyanides.

Potassium ferrocyanide[2] forms with Fe^{++} a white precipitate of $K_2FeFe(CN)_6$ (Eq. 2), insoluble in acids, transposed by the alkalis (Eq. 3). The precipitate is converted into Prussian blue (see below) gradually by exposure to the air, immediately by oxidizing agents (Eq. 4). With Fe^{+3}, ferric ferrocyanide (Eq. 5), $Fe_4[Fe(CN)_6]_3$, Prussian blue, is formed, insoluble in acids, decomposed by alkalis (Eq. 6). If the reagent is added in large excess, the precipitate is partially dissolved, forming a blue liquid. Strong acids should not be present, as they color the reagent blue.[3] Fluorides interfere, in that a white precipitate is formed.[4] The same is true in case of Turnbull's blue. In neutral solution, one part of Fe in 500,000 may be detected.[5] Ferrocyanides are transposed by NaOH and decomposed by fusion with $NaNO_3$ and Na_2CO_3, the Fe being obtained as Fe_2O_3.[6]

Potassium ferricyanide precipitates from dilute solutions of Fe^{++}, ferrous ferricyanide (Eq. 7),[7] $Fe_3[Fe(CN)_6]_2$ (Turnbull's blue), dark blue, insoluble in acids, transposed by alkali hydroxides (Eq. 8). With Fe^{+3} no precipitate is obtained, but the solution is colored brown or green[8] (Eq. 9). This is an important reagent for the detection of Fe^{++} in the presence of Fe^{+3}.[9] The solution should be diluted sufficiently to permit the detection of the precipitate of ferrous ferricyanide in the presence of the dark colored liquid due to any Fe^{+3} present. If no precipitate be obtained (indicating absence of Fe^{++}), a drop of $SnCl_2$ or other strong reducing agent constitutes a delicate test for Fe^{+3} and confirms the negative test for Fe^{++}.

Thiocyanate ion, CNS^-, gives no reaction with Fe^{++}; with Fe^{+3} blood red ferric thiocyanate, $Fe(CNS)_3$[10] (solution), is formed (Eq. 10). This constitutes a very delicate test for Fe^{+3}, one part in 1,600,000 giving a

[1] Gmelin, 8th ed., No. 59, p. 561.

[2] Regarding the question of iron ferro- and ferri-cyanides see: Friend, IX, 2, 202 *et seq.*, 225 *et seq.*

[3] The strong acids probably cause this effect by permitting decomposition of the reagent with formation of ferric ferrocyanide.

[4] Szebellédy, *Z. anal. Ch.*, **75**, 165–7 (1928).

[5] Wagner, *Z. anal. Ch.*, **20**, 350 (1881).

[6] Koningh, *Z. angew. Ch.*, **11**, 463 (1898).

[7] Claimed by some authorities to be identical with ferric ferrocyanide.

[8] Brown = fresh reagent; green = old solution.

[9] See also (**9**) the diacetyldioxime test.

[10] Schlesinger and van Valkenburgh, *J. Am. Ch. Soc.*, **53**, 1212–6 (1931), suggest that the red color is due to $Fe(CNS)_6^{-3}$, and that the salt formed is $FeFe(CNS)_6$.

perceptible pink.[1] Since the reaction is reversible, excess of the reagent is an important factor in the test, as is also the acidity.[2] The red salt is very soluble in water, alcohol and ether; being more soluble in ether than in water, it may be extracted and concentrated by use of that reagent, thus increasing the delicacy of the test. The red color is decreased or destroyed by $HgCl_2$,[3] phosphates, borates, acetates, oxalates, tartrates, citrates, etc., and acids of these salts. Strong oxidizing acids, e.g., HNO_3, $HClO_3$, etc., form red perthiocyanogen, $H(CNS)_3$.

(1) $FeCl_3 + 3\,KCN + 3\,H_2O = Fe(OH)_3 + 3\,KCl + 3\,HCN$

(2) $FeSO_4 + K_4Fe(CN)_6 = K_2FeFe(CN)_6 + K_2SO_4$

(3) $K_2FeFe(CN)_6 + 2\,KOH = Fe(OH)_2 + K_4Fe(CN)_6$

(4) $4\,K_2FeFe(CN)_6 + O_2 + 4\,HCl = Fe_4[Fe(CN)_6]_3 + K_4Fe(CN)_6 + 4\,KCl + 2\,H_2O$

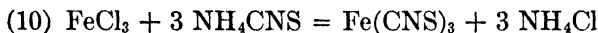
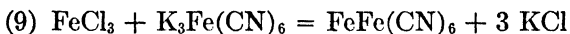
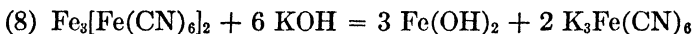
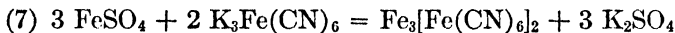
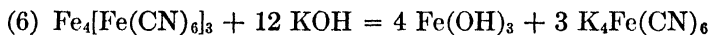
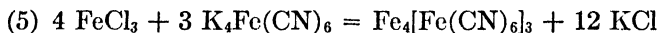
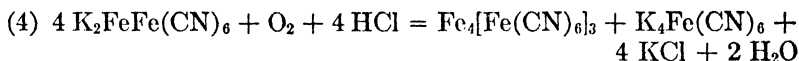
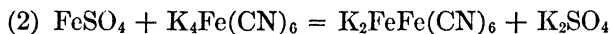
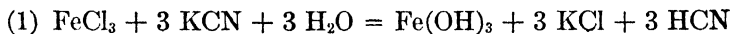
(5) $4\,FeCl_3 + 3\,K_4Fe(CN)_6 = Fe_4[Fe(CN)_6]_3 + 12\,KCl$

(6) $Fe_4[Fe(CN)_6]_3 + 12\,KOH = 4\,Fe(OH)_3 + 3\,K_4Fe(CN)_6$

(7) $3\,FeSO_4 + 2\,K_3Fe(CN)_6 = Fe_3[Fe(CN)_6]_2 + 3\,K_2SO_4$

(8) $Fe_3[Fe(CN)_6]_2 + 6\,KOH = 3\,Fe(OH)_2 + 2\,K_3Fe(CN)_6$

(9) $FeCl_3 + K_3Fe(CN)_6 = FeFe(CN)_6 + 3\,KCl$

(10) $FeCl_3 + 3\,NH_4CNS = Fe(CNS)_3 + 3\,NH_4Cl$

c. Nitric acid readily oxidizes all Fe^{++} salts to Fe^{+3}, the reaction being hastened by heat: $3\,FeCl_2 + 4\,HNO_3 = 2\,FeCl_3 + Fe(NO_3)_3 + NO + 2\,H_2O$. If the system is cold, and concentrated H_2SO_4 present, the so-called "brown ring" complex, $FeSO_4{\cdot}NO$, is obtained.[4]

d. Hypophosphorous acid reduces Fe^{+3} to Fe^{++}. Alkali phosphates, e.g., Na_2HPO_4, precipitate from solutions of Fe^{++} a mixture of $FeHPO_4$ and $Fe_3(PO_4)_2$, white to bluish white, soluble in mineral acids. If an alkali acetate is present, the precipitate consists of the tertiary phosphate alone: $3\,FeSO_4 + 2\,Na_2HPO_4 + 2\,NaC_2H_3O_2 = Fe_3(PO_4)_2 + 3\,Na_2SO_4 + 2\,HC_2H_3O_2$. With Fe^{+3}, phosphates form ferric phosphate, $FePO_4$, insoluble in acetic acid, readily soluble in more highly ionized acids, HCl, HNO_3, H_2SO_4. Hence Fe^{+3} is precipitated by H_3PO_4 in the presence of alkali acetates: $FeCl_3 + H_3PO_4 + 3\,NaC_2H_3O_2 = FePO_4 + 3\,NaCl + 3\,HC_2H_3O_2$. The alkali hydroxides transpose freshly precipitated $FePO_4$,

[1] Wagner, *Z. anal. Ch.*, **20**, 350 (1881).

[2] van Urk, *Ch. Weekblad*, **25**, 703–6 (1928), *C.A.* **23**, 1589, has considered the accuracy of the thiocyanate test for Fe^{+3} in the presence of various salts. He states that salts of weak acids have considerable influence.

[3] Due probably to the formation of the less dissociated $Hg(CNS)_2$ (or $Hg(CNS)_4^{--}$) which is colorless.

[4] See p. 476, 6, concerning details of the brown ring test.

forming $Fe(OH)_3$ and the corresponding alkali phosphate. The transposition is incomplete in the cold. Fixed alkali hydroxides, in excess, dissolve $AlPO_4$, thus effecting a separation from Fe. Ferric phosphate warmed with $(NH_4)_2S$, forms Fe_2S_3: $2\,FePO_4 + 3\,(NH_4)_2S = Fe_2S_3 + 2\,(NH_4)_3PO_4$.

e. Hydrosulfic acid is without action upon Fe^{++} in acid solution. Alkali sulfides form ferrous sulfide, FeS, black, insoluble in excess reagent, readily soluble in dilute acids with evolution of H_2S. The moist precipitate is slowly converted, in the air, to $FeSO_4$, and finally to a basic ferric sulfate, $Fe_2O(SO_4)_2$. Ferric salts are reduced to ferrous by H_2S or soluble sulfides in acid solution: $2\,FeCl_3 + H_2S = 2\,FeCl_2 + 2\,HCl + S$; ferric salts react with $(NH_4)_2S$ to form Fe_2S_3; Fe^{++} and $(NH_4)_2S_x$ also form Fe_2S_3. Ferrous sulfite is moderately soluble in water, readily soluble in excess H_2SO_3. The moist salt oxidizes rapidly on exposure to the air.[1] Ferric sulfite is only known as a red[2] solution, formed, e.g., by the action of SO_2 on freshly precipitated $Fe(OH)_3$; rapidly reduced to the ferrous condition: $Fe_2(SO_3)_3 = FeSO_3 + FeS_2O_6$. Ferrous thiosulfate, FeS_2O_3, is formed, together with some FeS and $FeSO_3$, by the action of SO_2 upon Fe°[3] or FeS.[4] Ferric ion is reduced to Fe^{++} by $Na_2S_2O_3$ in neutral solution: $2\,FeCl_3 + 2\,Na_2S_2O_3 = 2\,FeCl_2 + 2\,NaCl + Na_2S_4O_6$;[5] in acid solution H_2SO_4 and S are formed: $2\,FeCl_3 + Na_2S_2O_3 + H_2O = 2\,FeCl_2 + 2\,NaCl + H_2SO_4 + S$. Ferric ion is converted to a basic nitrate by the addition of $(NH_4)_2SO_4$ to a solution of Fe^{+3} in HNO_3, and evaporation to dryness; insoluble in H_2O (separation from Al).

f. Chlorides and bromides of both Fe^{++} and Fe^{+3} are of minor importance analytically. Fe^{+3} is reduced to Fe^{++} by HI, with liberation of iodine.

g. Soluble arsenites and arsenates precipitate neutral or faintly acid solutions of Fe^{++} and Fe^{+3}, forming the corresponding arsenites and arsenates. Basic ferric arsenite, $4Fe_2O_3{\cdot}As_2O_3{\cdot}5H_2O$ is formed when an excess of $Fe(OH)_3$ is added to H_3AsO_3. The product is insoluble in acetic acid. The same compound is formed when moist $Fe(OH)_3$ is given as an antidote in arsenic poisoning.[6]

h. Ferrous iron is rapidly oxidized to ferric by $Cr_2O_7^{--}$; with Fe^{+3} there is no reaction.

i. Zinc oxide (hydroxide) precipitates Fe^{+3}, Al^{+3}, Cr^{+3} and Cu^{++} completely, Pb^{++} partially, effecting a separation of these metals from Mn, Co and Ni.

[1] Seubert and Elten, *Z. anorg. allgem. Ch.*, **4**, 44 (1893).
[2] The red color may be due to colloidal $Fe(OH)_3$.
[3] Fordos and Gélis, *J. pharm. ch.*, [3] **4**, 333 (1843).
[4] Henderson and Weiser, *J. Am. Ch. Soc.*, **35**, 239 (1913).
[5] Fordos and Gélis, *Compt. rend.*, **15**, 920 (1842).
[6] A mixture of milk of magnesia, $Mg(OH)_2$, and $Fe_2(SO_4)_3$ is generally indicated.

7. Ignition. — The larger number of iron salts, in the solid state, are decomposed by heat; $FeCl_3$ vaporizes, partly decomposed, at slightly above 100°. Ignition in air changes Fe^{++} compounds, and ignition on charcoal or by a reducing flame, changes Fe^{+3} compounds to the magnetic oxide. Ferrous oxalate ignited in absence of air, gives pyrophoric iron (cf. 4). Ferric oxide, ignited in a current of hydrogen, gives Fe_3O_4 from 330° to 440°, FeO from 500° to 600°, and Fe° above 600°.[1] In the outer flame, the borax bead when moderately saturated with any compound of iron, acquires a reddish color while hot, fading and becoming light yellow when cold, colorless if only a small amount of Fe be present. The same bead, held persistently in the reducing flame, becomes colorless unless a large amount of iron is present, when it shows the pale green color of Fe^{++} compounds. The reactions with microcosmic salt are less distinct, but similar. Co, Ni, Cr and Cu interfere.

Ferric compounds, heated for a short time in a blue borax bead, i.e., containing a little CuO, leave the bead blue; Fe^{++} compounds so treated change the blue color to red, i.e., Cu_2O is formed.

8. Detection. — After removal of Groups I and II, the iron (now as Fe^{++}) is oxidized with HNO_3. Addition of NH_4Cl and a slight excess of NH_4OH precipitates $Fe(OH)_3$, $Al(OH)_3$ and $Cr(OH)_3$. The Al and Cr are removed by addition of an excess of $NaOH + H_2O_2$ and heating. The residue may be dissolved in HCl or H_2SO_4 and tested for Fe^{+3}: KCNS gives a blood red color; $K_4Fe(CN)_6$ a blue precipitate. The original solution must be tested to determine the initial condition of the iron. A portion of the original solution acidified with HCl gives a blood red color with CNS^- if Fe^{+3} is present (Hg^{++} and Cu^{++} interfere), no color with Fe^{++}. Another portion acidified with HCl and diluted somewhat gives a blue precipitate with $K_3Fe(CN)_6$ if Fe^{++} is present, only a brown or green color with Fe^{+3} (cf. §130).[2]

9. Determination. — *Gravimetric.* — Iron may be precipitated as $Fe(OH)_3$, ignited and weighed as Fe_2O_3. *Volumetric.* — Reduction of iron to Fe^{++} and titration with $K_2Cr_2O_7$ (using either $K_3Fe(CN)_6$ as an external indicator, diphenylamine as an internal indicator, or an electrometric method), is chiefly used, because the operation can be carried out in HCl solution. However, the titration of Fe^{++} with $KMnO_4$ in H_2SO_4 solution is very satisfactory. Ceric sulfate has also been suggested as the oxidizing agent.[3] Titanous salts may be used to titrate Fe^{+3}. *Colorimetric.* — Small amounts of iron may be determined by treating Fe^{+3} with CNS^- and comparing the red color obtained with that of a standard. Due to the many difficulties involved, the method is likely to give low results.[4] If Fe^{++} is treated with diacetyldioxime in NH_4OH solution, the red color developed is proportional to the amount of Fe^{++} present, hence this reaction may be used for the determination of iron.

10. Oxidation and Reduction. — Metallic iron precipitates the free metal from solutions of Au, Pt, Ag, Hg, Bi and Cu (separation from Cd).

Ferrous ion is changed to ferric by treating with a solution of Au, Ag^+, Cr^{+6}, Mn^{+7}, Mn^{+6}, or H_2O_2. Oxidation is effected in presence of some

[1] Moissan, *Ann. ch. phys.*, [5] **21**, 199 (1880).

[2] Gutzeit, *Helv. Ch. Acta*, **12**, 713–40 (1929), *C.A.* **23**, 4644, has summarized a number of tests for Fe, particularly those employing organic reagents.

[3] Willard and Young, *J. Am. Ch. Soc.*, **50**, 1334 (1928); Furman, *Ibid.*, **50**, 755 (1928).

[4] Lundell and Knowles, *J. Am. Cer. Soc.*, **11**, 122 (1928); cf. Stokes and Cain, *J. Am. Ch. Soc.*, **29**, 409 (1907).

dilute acid, such as H_2SO_4 or H_3PO_4, by PbO_2, Pb_3O_4, Mn_3O_4, MnO_2, Mn_2O_3, Co_2O_3, or NiO_2. The following acids oxidize Fe^{++} to Fe^{+3}: HNO_2, HNO_3, $HClO$, $HClO_2$, $HClO_3$, H_2SO_4 (if concentrated and hot), $HBrO$, $HBrO_3$ and HIO_3. Bromine and chlorine, in the presence of NaOH, change Fe^{++} and Fe^{+3} to perferrate, FeO_4^{--}. Barium perferrate is the most stable of these compounds. They are strong oxidizing agents, acting upon nitrites, tartrates, glycerol, alcohol, ether, ammonia, etc.

Ferric ion is reduced to ferrous by Sn^{++}, Cu_2^{++}, H_3PO_2, H_3PO_3, H_2S, H_2SO_3, $Na_2S_2O_3$, or HI; also by "nascent" hydrogen, or any of the metals that produce hydrogen when treated with acids, including Pb, Sn, Cd, Fe, Al, Co, Ni, Zn and Mg; also by As, Sb, Bi and Cu.

§127. Outline of the Analysis of Group III
(Starting with the filtrate from Group II)

Metals, after removal of Groups I–II, whose hydroxides precipitate with **slight** excess of NH_4OH in the presence of high concentration of NH_4Cl.

Metals	Fe	Cr	Al
Ions in acid solution	Fe^{++} Fe^{+3}	Cr^{+3} $Cr_2O_7^{--}$	Al^{+3}
Ions in NaOH solution	——	CrO_2^{-} CrO_4^{--}	AlO_2^{-}
Ions in NH_4OH solution	——	CrO_4^{--}	——

Boil out H_2S, oxidize Fe^{++} if present, make 3–4 N with NH_4Cl

Fe^{+3}	Cr^{+3}	Al^{+3}
	NH_4OH	
$\underline{Fe(OH)_3}$	$\underline{Cr(OH)_3}$	$\underline{Al(OH)_3}$
	$NaOH + H_2O_2$	
$\underline{Fe(OH)_3}$	Na_2CrO_4	$NaAlO_2$
H_2SO_4	NH_4Cl	
$Fe_2(SO_4)_3$	Na_2CrO_4	$\underline{Al(OH)_3}$
KCNS	H_2SO_4	HCl
$Fe(CNS)_3$	$Na_2Cr_2O_7$	$AlCl_3$
	H_2O_2	Aluminon Reagent $+ NH_4C_2H_3O_2 + NH_4OH$
	H_3CrO_8	$\underline{Al(OH)_3}$ (red lake)

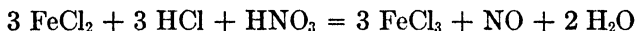
DIRECTIONS FOR THE PRECIPITATION AND ANALYSIS OF THE THIRD GROUP

§**128**. In the directions given below it is assumed that Groups I and II have been present and removed in the usual manner, the final filtrate being used for the precipitation of Group III. If one wishes to examine a solution directly for Group III, with Groups I and II known to be absent, account must be taken of the forms in which the Group III metals may be present. For satisfactory precipitation with NH_4OH all three of the metals must be present as trivalent cations. Therefore tests for the other forms must be applied and adequate steps taken to convert them to the proper ions before precipitating Group III. If the solution is acid, Fe^{++} may be identified by the $K_3Fe(CN)_6$ test and oxidized to Fe^{+3} by HNO_3. If Fe^{++} is absent Cr^{VI} may be identified by the "vanishing blue" test, and reduced to Cr^{+3} by $CH_2O + HCl$. Aluminate ion, found only in alkaline solution, is changed to Al^{+3} by acidifying with HCl. If MnO_4^- or MnO_4^{--} is present, as judged by color, it should be reduced by $CH_2O + HCl$.

Manipulation. — Boil the filtrate from the second group (§80) until the H_2S is completely removed (test fumes with $Pb(C_2H_3O_2)_2$ paper), then test for Fe^{++} as follows: Take 2–3 cc. of the solution in a separate test tube, add 8–10 cc. of H_2O and a few drops of $K_3Fe(CN)_6$. If Fe^{++} is present a blue precipitate will form.

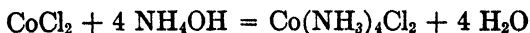
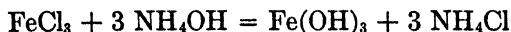
$$3\ FeCl_2 + 2\ K_3Fe(CN)_6 = Fe_3[Fe(CN)_6]_2\ (\text{blue}) + 6\ KCl$$

If the test is positive add 5 cc. of HCl and 1–2 cc. of HNO_3, heat to boiling and let boil gently until the Fe^{++} is completely oxidized.

$$3\ FeCl_2 + 3\ HCl + HNO_3 = 3\ FeCl_3 + NO + 2\ H_2O$$

If no Fe^{++} was found after boiling out the H_2S, the solution is ready for the next operation.

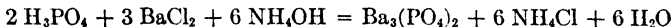
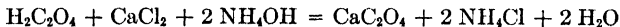
Add to the solution from one to two times its volume of 5 N NH_4Cl, heat to boiling, and add NH_4OH a few drops at a time, with stirring, until the solution has a faint odor of ammonia. Boil gently about 1 minute, let settle 1–2 minutes, then filter and wash with hot 1% NH_4Cl. Group III metals precipitate as hydroxides; Co, Ni and Zn stay in solution as complex-ammonia ions; and the other metals of later groups stay in solution as simple metallic ions.

$$FeCl_3 + 3\ NH_4OH = Fe(OH)_3 + 3\ NH_4Cl$$

$$CoCl_2 + 4\ NH_4OH = Co(NH_3)_4Cl_2 + 4\ H_2O$$

The precipitate is analyzed for Group III (§130), and the filtrate is reserved for later groups (§138).

§129. **Notes.** — 1. Occasionally an unknown contains acid radicals that interfere with the separation of Group III from later group metals by the procedure given above. Thus, if oxalic or phosphoric acid is present there will precipitate oxalates or phosphates of some of the later group metals when the solution is neutralized with NH_4OH.

$$H_2C_2O_4 + CaCl_2 + 2\,NH_4OH = CaC_2O_4 + 2\,NH_4Cl + 2\,H_2O$$

$$2\,H_3PO_4 + 3\,BaCl_2 + 6\,NH_4OH = Ba_3(PO_4)_2 + 6\,NH_4Cl + 6\,H_2O$$

Or if tartaric or citric acid is present soluble complex ions may form with the Group III metals such that the hydroxides do not precipitate on the addition of NH_4OH. In such cases special procedures are introduced. These are discussed more fully in §§145–153.

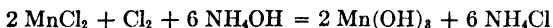
2. It is necessary to remove H_2S, otherwise Group IV sulfides would precipitate on the addition of NH_4OH.

3. The presence of HNO_3 in the solution may result in partial oxidation of H_2S to S and even to H_2SO_4. If Ba or Sr is present a finely divided white precipitate of $BaSO_4$ or $SrSO_4$ may separate during this operation. If such a precipitate is obtained it should be filtered out and tested for Ba and Sr (§192).

4. Any iron that may have been present in the ferric condition is reduced to Fe^{++} while precipitating Group II with H_2S. Sometimes this is reoxidized at the end of the process of boiling out H_2S (see note 3), frequently the iron is still left in the ferrous condition. Since Fe^{++} does not precipitate completely with NH_4OH while Fe^{+3} does, it is necessary to oxidize any Fe^{++} to Fe^{+3} before precipitating Group III.

5. It is more satisfactory to test for Fe^{++} and oxidize it if present than to insert a routine manipulation of adding HNO_3 and boiling: (*a*) The routine procedure may fail unless tests are applied to make sure that the Fe^{++} is completely oxidized, (*b*) it is unnecessary to boil with HNO_3 unless Fe^{++} is present, and (*c*) boiling with HNO_3, when unnecessary, may set Cl_2 free in the solution so that when Group III is precipitated Mn^{++} is oxidized and precipitated as $Mn(OH)_3$ or MnO_2.

$$HNO_3 + 3\,HCl = Cl_2 + NOCl + 2\,H_2O$$

$$2\,MnCl_2 + Cl_2 + 6\,NH_4OH = 2\,Mn(OH)_3 + 6\,NH_4Cl$$

It is true, however, that if one is looking for very small amounts of Fe the test for Fe^{++} may fail since only a small fraction of the solution is being tested, and yet sufficient Fe may be present to be precipitated and identified in Group III. This case should only arise when the amount of Fe present is less than 1–2 mg.

6. In oxidizing Fe^{++} to Fe^{+3} it is desirable to use as little HNO_3 as can conveniently be done so as to decrease the amount of Mn carried down in Group III (see note 5, *c*). On the other hand it is necessary to make sure that the Fe^{++} is completely oxidized (by negative test for Fe^{++} on a portion of the solution), otherwise some Fe may carry over into Group IV and cause trouble there.

7. The separation of Group III from Group IV is very unsatisfactory if small amounts of NH_4Cl and large excess of NH_4OH are used. Thus Co, Ni and Zn may be largely adsorbed by the third group hydroxides and Mn oxidized by O_2 from the air and precipitated as $Mn(OH)_3$ under such conditions. But by increasing the concentration of NH_4Cl in the solution to 3–4 *N* and using NH_4OH in very slight excess the separation is remarkably improved. Thus a precipitate of $Al(OH)_3$ formed in the presence of Co is only light pink, while a solution of Mn^{++} under such conditions may stand for some time without marked precipitation.

If the volume of the solution is already large, further dilution may be avoided by adding the solid NH_4Cl instead of the solution. In such a case use 1.5–2 g. of the salt for each 10 cc. of solution.

8. If Cr^{+3} is treated with excess of NH_4OH in the cold a soluble complex chromic-ammonia compound, of lavender to red color, is formed which is only slowly converted to $Cr(OH)_3$ on boiling. On the other hand, if the solution is hot when the NH_4OH is added, $Cr(OH)_3$ precipitates directly.

9. Large excess of NH_4OH should be avoided because $Al(OH)_3$ is appreciably soluble in excess of NH_4OH, and Mn^{++} is oxidized fairly readily if the solution becomes more than faintly alkaline.

10. The hydroxides of Group III are very gelatinous when freshly precipitated, being hard to filter and wash. On standing a short time in contact with the hot solution they become more flocculent and easier to handle.

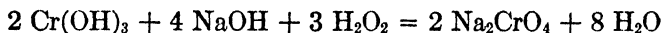
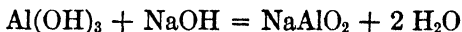
11. Washing with distilled water may cause these hydroxides to become colloidal and run through the filter paper. Using NH_4Cl in the wash water prevents this.

12. Tin and Pb, incompletely precipitated in Group II (§81, 8), may be precipitated in Group III as white hydroxides, somewhat resembling $Al(OH)_3$ in chemical behavior.

13. The Group V metals, Ba, Sr and Ca, sometimes precipitate partially in Group III as carbonates, due to $(NH_4)_2CO_3$ in the NH_4OH and to absorption of CO_2 from the air by the alkaline solution. This effect is slight, however, if the solution contains adequate amounts of NH_4Cl and is treated with only a slight excess of NH_4OH.

§130. **Manipulation.** — Transfer the precipitate (§128), consisting of hydroxides of the third group, to a casserole, add 5–10 cc. of 5 *N* NaOH and 3–5 cc. H_2O_2, heat to boiling and keep near the boiling point for 1–2 minutes. $Al(OH)_3$ and $Cr(OH)_3$ are dissolved, the latter being oxidized fairly rapidly to yellow CrO_4^{--}.

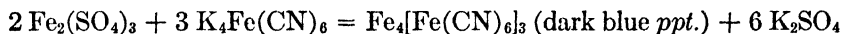
$$Al(OH)_3 + NaOH = NaAlO_2 + 2\ H_2O$$

$$2\ Cr(OH)_3 + 4\ NaOH + 3\ H_2O_2 = 2\ Na_2CrO_4 + 8\ H_2O$$

Ferric hydroxide remains as a precipitate.

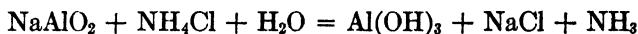
Dilute with water to 20–25 cc., filter, and wash 2–3 times with distilled water. Reserve the filtrate to test for Cr and Al.

Dissolve the precipitate in 3–5 cc. of 5 *N* H_2SO_4, and test for Fe^{+3} by adding a few drops of $K_4Fe(CN)_6$ or of KCNS.

$$2\ Fe_2(SO_4)_3 + 3\ K_4Fe(CN)_6 = Fe_4[Fe(CN)_6]_3 \text{ (dark blue } ppt.) + 6\ K_2SO_4$$

$$Fe_2(SO_4)_3 + 6\ KCNS = 2\ Fe(CNS)_3 \text{ (dark red } solution) + 3\ K_2SO_4$$

To the filtrate containing CrO_4^{--} and AlO_2^- add 10–15 cc. of 5 *N* NH_4Cl, heat to boiling and continue boiling until only a faint odor of NH_3 persists. Excess of H_2O_2 is thus decomposed and Al precipitated as $Al(OH)_3$.

$$2\ H_2O_2 = 2\ H_2O + O_2$$

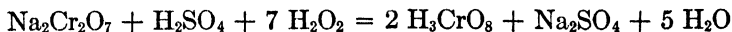
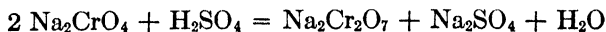
$$NaAlO_2 + NH_4Cl + H_2O = Al(OH)_3 + NaCl + NH_3$$

Filter and wash, reserving the filtrate to test for Cr.

Dissolve the precipitate (or as much as will dissolve readily) in 5 cc. of 1 *N* HCl, add 5 cc. of 3 *N* $NH_4C_2H_3O_2$ and 5 cc. of 0.1% solution of the ammonium salt of the organic compound, aurin tricarboxylic acid, shake, and then add NH_4OH until the solution is distinctly alkaline. A bright red flocculent precipitate indicates Al.

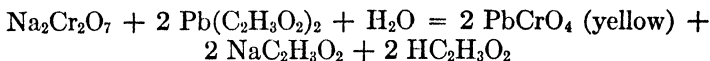
Tests for Cr are applied on the above filtrate as follows: (*a*) To half of the solution add 5 *N* H_2SO_4 until the solution is barely acid plus 1–2 cc.

excess, cool thoroughly, and then add 1 cc. of H_2O_2. If Cr is present a blue color will develop (disappearing again more or less promptly).

$$2\ Na_2CrO_4 + H_2SO_4 = Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

$$Na_2Cr_2O_7 + H_2SO_4 + 7\ H_2O_2 = 2\ H_3CrO_8 + Na_2SO_4 + 5\ H_2O$$

(*b*) To the rest of the solution add $HC_2H_3O_2$ until the solution is distinctly acid, then add 1–2 cc. of $Pb(C_2H_3O_2)_2$.

$$2\ Na_2CrO_4 + 2\ HC_2H_3O_2 = Na_2Cr_2O_7 + 2\ NaC_2H_3O_2 + H_2O$$

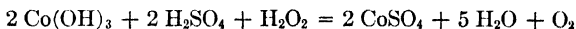
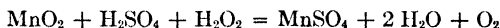
$$Na_2Cr_2O_7 + 2\ Pb(C_2H_3O_2)_2 + H_2O = 2\ PbCrO_4\ \text{(yellow)} + 2\ NaC_2H_3O_2 + 2\ HC_2H_3O_2$$

§**131. Notes.** — 1. Incomplete oxidation of Cr may result in the formation of a reddish-brown ppt. of $Cr_2(CrO_4)_3$, looking much like $Fe(OH)_3$. If the amount of Cr appears to be large it may be desirable to add more H_2O_2 and let the reaction continue a few minutes longer. Or the precipitate filtered out may be dissolved in dilute HCl, and the solution treated with excess NaOH and H_2O_2. The precipitate thus obtained is tested for Fe, and the filtrate is combined with the first filtrate to test for Cr and Al.

2. The purpose of diluting with water before attempting to filter is to cool the solution and reduce the concentration of NaOH sufficiently so that the filter paper will not be disintegrated. If trouble is still encountered, the solution may be diluted somewhat more and two filter papers folded together instead of one.

3. Group IV metals carried down in Group III are chiefly found with the $Fe(OH)_3$, though small amounts of Zn may go into solution as ZnO_2^{--} along with AlO_2^- and CrO_4^{--}.

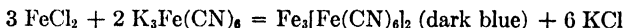
If the ppt. where $Fe(OH)_3$ is expected does not dissolve readily on warming with dilute H_2SO_4, add a few drops of H_2O_2 to reduce any MnO_2, $Co(OH)_3$ or NiO_2.

$$MnO_2 + H_2SO_4 + H_2O_2 = MnSO_4 + 2\ H_2O + O_2$$

$$2\ Co(OH)_3 + 2\ H_2SO_4 + H_2O_2 = 2\ CoSO_4 + 5\ H_2O + O_2$$

MnO_2 dissolves very readily, $Co(OH)_3$ and NiO_2 less readily. Tests may be applied for these metals by dividing the solution into several parts and trying the confirmatory reactions used in Group IV (§§140–143).

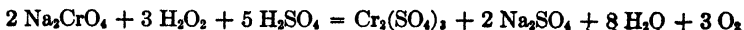
4. Dilute H_2SO_4 is used to dissolve the $Fe(OH)_3$ rather than HNO_3 or HCl because of the danger of oxidizing effects interfering with the confirmatory tests for iron. Under extreme conditions oxidation of $K_4Fe(CN)_6$ to $K_3Fe(CN)_6$ may prevent the test from showing, while with KCNS a red colored compound may form and be mistaken for $Fe(CNS)_3$. (The oxidizing action in the case of HCl would be due to the presence of MnO_2, etc., oxidizing some of the HCl to Cl_2.)

5. In the original solution Fe is present as Fe^{++} or Fe^{+3}. These will be found only in neutral or acid solutions, and are identified by tests on small portions of the original solution. For Fe^{++} take 1–2 cc. of the solution, add a few drops of HCl, dilute to 10 cc., and add a few drops of $K_3Fe(CN)_6$.

$$3\ FeCl_2 + 2\ K_3Fe(CN)_6 = Fe_3[Fe(CN)_6]_2\ \text{(dark blue)} + 6\ KCl$$

To test for Fe^{+3}, take 1–2 cc. of the solution, add a few drops of HCl, then try the same reagents as used in the final test for Fe^{+3} in Group III.

6. Since the test for Fe^{+3} is rather delicate, and Fe is commonly present in slight amounts in most materials unless they have been prepared and preserved with unusual care, one may consider a faint test to indicate only normal impurities in other substances present rather than an intentional constituent present in moderate quantity.

7. It is necessary to boil the alkaline solution several minutes in order to decompose the excess of H_2O_2. If this is not done small amounts of CrO_4^{--} will be reduced to Cr^{+3} on acidifying and the test for Cr will fail.

$$2\ Na_2CrO_4 + 3\ H_2O_2 + 5\ H_2SO_4 = Cr_2(SO_4)_3 + 2\ Na_2SO_4 + 8\ H_2O + 3\ O_2$$

There is no direct way to test for completeness of decomposition of H_2O_2, although one may observe a change in the way in which the solution boils when decomposition is almost complete. Thus, while appreciable quantities of H_2O_2 are still present the bubbles of O_2 prevent superheating and the solution boils smoothly; but when the O_2 bubbles no longer form freely the effects of local superheating are observed, the steam bubbles form somewhat irregularly and expand with mildly explosive violence, producing the effect commonly spoken of as "bumping." Also, in the procedure described above (§130) the time required to boil out the excess of NH_3 is sufficient to decompose the H_2O_2 effectively.

8. In using NH_4Cl to precipitate $Al(OH)_3$ directly from the alkaline solution it is necessary to add an amount distinctly more than equivalent to the NaOH used in the first step in the analysis of the third group precipitate. If the concentrations of the reagents are definitely known and the quantities used are measured, this is quite simple. Thus, if both reagents are 5 *N*, and 5 cc. of NaOH were used at the start, 10 cc. of NH_4Cl will be ample; or if 10 cc. of NaOH were used, 15 cc. of NH_4Cl should be employed. Since the reagents are not always made up accurately, it is usually worth while to test for excess of NH_4Cl by noting that after the solution has been boiled until it has only a slight odor of NH_3 it is only faintly alkaline and the odor does not become strong again on adding 1–2 cc. more of NH_4Cl. There is an advantage in precipitating $Al(OH)_3$ from the alkaline solution rather than acidifying and then adding NH_4OH or $(NH_4)_2CO_3$ (as frequently recommended), due to the fact that the gelatinous precipitate obtained is less transparent and thus more readily visible than that obtained from an acid solution.

9. A slight white precipitate is usually obtained where $Al(OH)_3$ is expected even when Al is not present. This is chiefly H_2SiO_3, derived from the NaOH used. The glass reagent bottle is attacked appreciably by the NaOH, forming a very dilute solution of Na_2SiO_3. The concentration of this is increased slightly by reaction of the NaOH with the beaker or casserole in which the Group III separations are carried out. On treatment with NH_4Cl the Na_2SiO_3 forms a white precipitate of H_2SiO_3.

$$Na_2SiO_3 + 2\ NH_4Cl = H_2SiO_3 + 2\ NaCl + 2\ NH_3$$

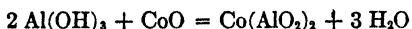
The white precipitate usually contains a very small amount of $Al(OH)_3$, so it is desirable to run a "blank test" to make allowance for this in judging the unknown. This is done as follows: Take 5–10 cc. of NaOH in the beaker or casserole, add 2–3 cc. of H_2O_2, boil 2–3 minutes, dilute to 20–25 cc. with water, filter, add 10–15 cc. of NH_4Cl to the filtrate, and boil until only a faint odor of NH_3 persists. Let settle, and note the amount of precipitate obtained. Filter and apply the confirmatory test for Al. In examining an unknown, do not report Al unless the test is definitely stronger than that given by the "blank test."

10. The chemistry of the confirmatory test for Al is not a simple reaction between the Al and the reagent added, but is an obscure effect of the type commonly called adsorption or lake-formation. It is more sensitive to change of conditions than ordinary reactions, therefore the directions given must be followed rather closely to obtain the best results.

An orange, or light red precipitate obtained on adding the reagent to the acid solution is due to action of the acid on the reagent. This precipitate dissolves in NH_4OH. The characteristic Al ppt. is not obtained until the solution is made alkaline.

11. Small amounts of Pb or Sn, incompletely precipitated in Group II, may show up as hydroxides in the white precipitate. They do not interfere, however, with the confirmatory test for Al.

12. An older confirmatory test for Al frequently recommended is as follows: Dissolve the precipitate of $Al(OH)_3$ in HCl, add a few drops of $Co(NO_3)_2$ solution, reprecipitate $Al(OH)_3$ (carrying a little Co with it) with NH_4OH, filter, wash, tear out the tip of the filter carrying the precipitate, wrap this in a platinum wire and burn in the flame, continuing the heating for a short time after the carbon of the paper has burned completely. Let cool and look for a blue colored residue of $Co(AlO_2)_2$.

$$2\ Al(OH)_3 + CoO = Co(AlO_2)_2 + 3\ H_2O$$

13. Aluminum is found in the original solution commonly as Al^{+3} or AlO_2^-. (The latter is frequently written AlO_3^{-3} or $H_2AlO_3^-$.) Testing the solution with litmus serves

to distinguish between them. If the solution is acid only Al^{+3} could be present; if strongly alkaline, AlO_2^-.

14. If CrO_4^{--} is present in significant amount the filtrate from $Fe(OH)_3$ will be yellow in color. If it is colorless there is less than 1 mg. of Cr in the solution.

15. The color produced in acid solution by the action of H_2O_2 on $Cr_2O_7^{--}$ disappears so promptly (due to instability of the H_3CrO_8) that this is usually called the " vanishing blue " test for Cr. Under unfavorable conditions (warm solution, high acidity, large amount of H_2O_2 added) the test becomes worthless; but with care (have solution cold, add not more than 1–2 cc. of free 5 *N* H_2SO_4 in 10 cc., and add the H_2O_2 a few drops at a time) the color will appear and persist for several seconds with even less than 1 mg. of Cr present. The color can be made more permanent by adding a layer of ether to the solution first. Then add the H_2O_2 and shake. The perchromic acid dissolves in the ether and is more stable there than in the aqueous solution.

16. If one desires to test for Zn in the solution containing CrO_4^{--}, the solution may be acidified with acetic acid and treated with excess of $BaCl_2$ to precipitate Cr as $BaCrO_4$. After filtering, the filtrate is treated with H_2S.

$$Zn(C_2H_3O_2)_2 + H_2S = ZnS \text{ (white)} + 2\,HC_2H_3O_2$$

17. The four common ions of Cr are Cr^{+3}, CrO_2^-, CrO_4^{--} and $Cr_2O_7^{--}$. These have different colors, Cr^{+3} blue green, CrO_2^- green, CrO_4^{--} yellow, and $Cr_2O_7^{--}$ orange; but in the presence of other colored substances it may be necessary to apply special tests to distinguish between them. Thus, try the vanishing blue test on the original solution (acidifying first if the solution is alkaline). If the test is negative, neither CrO_4^{--} nor $Cr_2O_7^{--}$ is present. Next note the reaction of the solution to litmus. If acid the solution may contain Cr^{+3} or $Cr_2O_7^{--}$, if alkaline CrO_2^- or CrO_4^{--}. CrO_4^{--} may also be found in neutral solution.

THE ZINC GROUP (FOURTH GROUP)

COBALT, NICKEL, MANGANESE AND ZINC

§132. Cobalt (Greek *kobalos*[1] = gnome). Co = 58.94. Atomic No. 27. Valence 2 and 3. First prepared by Brandt in 1735.

1. **Physical Properties.** — Density, 8.8;[2] melting point, 1480°;[3] boiling point, 2900°. Cobalt is similar to iron in appearance, harder and stronger than Fe or Ni. It is not very malleable. However, a small amount of carbon markedly increases the malleability and ductility. The fine powder oxidizes rapidly on exposure to air. At a white heat, cobalt burns rapidly to Co_3O_4. Like iron it is magnetic, but loses this property above 1150°. The chief alloys of Co are: (1) " stellite," a very hard Co-Cr alloy used as a cutting edge for tool steel; (2) " carboloy," a tungsten carbide containing a large amount

[1] Or M.H.G. *Kobold.*

[2] Biltz, *Z. anorg. allgem. Ch.*, **134**, 35 (1924).

[3] B. Stds. Cir. 35.

of Co, much harder,[1] and used for the same purpose; (3) a Co-Fe alloy containing 35% Co, used extensively as a magnet steel. Much cobalt is used to color enamels and glass blue, and as an accelerator in the oxidation of certain oils.

2. Occurrence. — Cobalt is not found in a free state except in meteorites. The principal ores are smaltite, $CoAs_2$; cobaltite, CoAsS; erythrite, $Co_3(AsO_4)_2 \cdot 8H_2O$; linnaeite, Co_3S_4. Generally cobalt is associated with iron, nickel, copper and silver minerals. The principal sources are the "cobalt district" of Canada and the Belgian Congo. The total annual production is about 800 tons, approximately half coming from each of the two sources. The price of the metal per pound is $2 to $2.50.

3. Preparation. — (*a*) The ore is smelted in a small blast furnace to obtain a speiss consisting of the arsenides of Co, Ni, Cu, Fe and Ag. This speiss is pulverized, mixed with NaCl, and roasted. The soluble chlorides are leached out and the Cu removed with Fe. Fractional precipitation with $Ca(OH)_2$ removes the Fe, and addition of NaClO gives $Co(OH)_3$, which can be ignited to Co_3O_4. This oxide may be reduced to the metal by heating with carbon. (*b*) The cobaltiferous copper ore of the Belgian Congo is smelted for Cu. The slag is smelted to produce a Cu-Co-Fe alloy, which is dissolved in H_2SO_4. The solution thus obtained may be treated as above to recover the Co.

4. Oxides and Hydroxides.[2] — Cobaltous oxide, CoO, gray to greenish, is obtained, (*a*) by careful reduction of the higher oxides in hydrogen (a little metallic Co may be formed); (*b*) by igniting the hydroxide or carbonate;[3] (*c*) by heating the higher oxides above 1000°. Cobaltous hydroxide, $Co(OH)_2$, is obtained from cobaltous salts by precipitation with fixed alkali. The precipitate first formed is blue. It oxidizes on exposure to air; turns pink if warmed.[4] The most stable oxide is tricobalt tetroxide, Co_3O_4. It is made by heating any of the oxides or hydroxides, the carbonate, oxalate, or nitrate, to a dull red in the air. Several more complex oxygen compounds have been reported, e.g., $Co_3O(OH)_6$ (which may be the hydrate, $Co_3O_4 \cdot 3H_2O$). Cobaltic oxide, Co_2O_3, black, is made by heating the nitrate to about 180°. Cobaltic hydroxide, $Co(OH)_3$, is made by treating Co^{++} with ClO^-, Br_2 or I_2 in the presence of a fixed alkali or alkali carbonate. Upon ignition in air, $Co(OH)_3$ forms Co_3O_4. It dissolves in HCl with the evolution of chlorine (possibly Cl_2O); in H_2SO_4, with liberation of oxygen, forming Co^{++}. Cobalt peroxide, CoO_2, has been reported.[5,6,7]

5. Solubilities. — *a. Metal.* — Slowly soluble on warming in dilute HCl or H_2SO_4, more rapidly in HNO_3; not oxidized on exposure to air or when heated in contact with alkalis unless in powder form. Like Fe, it may exist in a passive state. The halogens form Co^{++} compounds.

b. Oxides and Hydroxides. — Cobaltous oxide (gray-green), and hydroxide (rose-red), are insoluble in water; soluble in acids, in NH_4OH, and in concentrated solutions of the fixed alkalis when heated. The various higher oxides and hydroxides are insoluble in NH_4OH or NH_4Cl (separation from $Ni(OH)_2$ after treatment with iodine in alkaline mixture); decomposed by acids, evolving O_2 with non-reducing acids, or a halogen from the halogen acids, with formation of Co^{++} salts. Co_3O_4 is not readily soluble in acids.

c. Salts. — Cobalt forms two classes of salts: cobaltous, Co^{++}, derived from CoO; and cobaltic, Co^{+3}, from Co_2O_3. The latter are quite unstable,

[1] It will readily cut glass.

[2] Natta and Strada, *Gazz. ch. ital.*, **58**, 419–33 (1928), *C.A.* **23**, 783, have made a careful study of the oxides and hydroxides of Co.

[3] LeBlanc and Möbius, *Z. physik. Ch.*, **142A**, 151–76 (1929), *C.A.* **23**, 4417, say that CoO is best prepared by decomposition of the carbonate in vacuum at 320°–460°.

[4] Hantzsch, *Z. anorg. allgem. Ch.*, **73**, 304–8 (1911), states that $Co(OH)_2$ is pink and $CoO \cdot H_2O$ is blue.

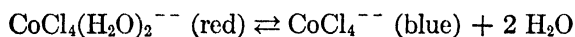
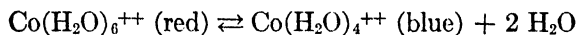
[5] Metzl, *Z. anorg. allgem. Ch.*, **86**, 358 (1914).

[6] Natta and Strada, *Gazz. ch. ital.*, **58**, 419–33 (1928), *C.A.* **23**, 783, found only three oxides of Co — CoO, Co_3O_4 and Co_2O_3 — and one hydroxide, $Co(OH)_2$. They believe that $Co(OH)_3$ is hydrated Co_2O_3.

[7] For an extensive bibliography on the colors of Co oxides, see: Witteveen and Farnau, *Ind. Eng. Ch.*, **13**, 1061–6 (1921).

decomposing in most cases at ordinary temperatures to form cobaltous salts. The cobaltous salts show a remarkable variation in color. The crystallized salts are pink; the anhydrous salts are blue. Dilute solutions are pink. When concentrated or in the presence of a strong acid, the color is generally blue. Several explanations have been offered. Howell[1] believes that the change is probably due to dehydration of the Co atom:

$$Co(H_2O)_6^{++} \text{ (red)} \rightleftarrows Co(H_2O)_4^{++} \text{ (blue)} + 2\ H_2O$$

$$CoCl_4(H_2O)_2^{--} \text{ (red)} \rightleftarrows CoCl_4^{--} \text{ (blue)} + 2\ H_2O$$

i.e., the number of groups surrounding the Co atom is six when red, four when blue.

Cobaltous nitrate and acetate are deliquescent; the chloride, hygroscopic; the sulfate, efflorescent. The chloride vaporizes, undecomposed, at a high temperature. The carbonate, sulfide, phosphate, borate, oxalate, cyanide, ferrocyanide and ferricyanide are insoluble in water. The ammonio-cobaltous compounds and the double cyanides of cobalt with the alkali metals are soluble in water. Most of the salts insoluble in water are soluble in NH_4OH.[2]

6. **Reactions.** — *a.* The fixed alkali hydroxides precipitate, from solutions of Co^{++} salts, blue basic salts, that absorb oxygen from the air and turn gray green, as cobalto-cobaltic hydroxide; or if boiled before oxidation, become rose red, as cobaltous hydroxide, $Co(OH)_2$. The precipitate is slightly soluble in hot, concentrated KOH, giving a blue colored solution (distinction from Ni). Freshly precipitated $Pb(OH)_2$, $Zn(OH)_2$ and HgO precipitate $Co(OH)_2$ from solutions of Co^{++} salts at 100°. The presence of NH_4Cl, non-volatile organic acids, or sugar prevents the precipitation of Co^{++} by the alkalis. Ammonium hydroxide, in the absence of ammonium salts, etc., produces the same precipitate as the fixed alkalis; incomplete, even at first, due to the effect of the NH_4^+ released during the reaction; soluble in excess of NH_4OH to give a solution that turns brown due to oxidation, and is not affected by NaOH. Chloropentammine cobaltichloride, $Co(NH_3)_5ClCl_2$, is obtained when an ammoniacal solution of Co^{++} is oxidized. It is only slightly soluble in concentrated HCl. The formation of this compound may be used to separate Co^{++} from Ni^{++}. The great stability of this complex is indicated by the fact that the NH_3 is not removed by acid. Only two-thirds of the chlorine is precipitated

[1] Howell, *J. Ch. Soc.*, **1929**, 162–72; **1927**, 158; Hill and Howell, *Phil. Mag.*, **48**, 833 (1924), (includes a good account of previous work on the problem). Bassett and Croucher, *J. Ch. Soc.*, **1930**, 1784–1819, state that neither the simple dehydration theory nor the variable coördination theory of the color changes is supported by the data.

[2] A discussion of the cobalt ammines is beyond the scope of this book. For a survey of the literature, see: Gmelin, 8th ed., No. 58 (1930); Friend, X, (1928).

by Ag^+.[1] If Co^{++} is treated with NaOH (not NH_4OH), and an oxidizing agent (Br_2, NaClO, $S_2O_8^{--}$, H_2O_2, etc.), a brown to black precipitate of $Co(OH)_3$ is obtained. It does not redissolve in $NH_4OH + NH_4Cl$, or in NaCN. In this latter case, excess NiO_2 promotes solution of the $Co(OH)_3$ (distinction from Ni).

Alkali bicarbonates, containing free CO_2, precipitate red $CoCO_3 \cdot 6H_2O$ at room temperature, the blue anhydrous salt near the boiling point. Normal carbonates precipitate basic cobalt carbonate. The precipitate is soluble in $(NH_4)_2CO_3$ or NH_4Cl, but very slightly soluble in the fixed alkali carbonates. Carbonates of Ba, Sr, Ca, or Mg do not precipitate Co^{++} in the cold (separation from Fe^{+3}, Al^{+3} and Cr^{+3}), but by prolonged boiling it is completely precipitated (probably due to oxidation). However, if Co^{++} is treated with Cl_2, Co^{+3} is formed, which is precipitated in the cold on digestion with $BaCO_3$ (distinction from Ni). If a solution of Co^{++} is saturated with $NaHCO_3$ by addition of a slight excess of the solid salt and then treated with H_2O_2, an apple green cobaltic product is obtained (distinction from Ni), the composition of which is unknown.[2] The test will detect 0.025 mg. of Co in 10 cc. of solution.

b. Oxalic acid and oxalates precipitate reddish cobaltous oxalate, CoC_2O_4. At first only a cloudiness is obtained, then finally complete precipitation. The salt is soluble in mineral acids and NH_4OH.

Alkali cyanides — as NaCN — precipitate the brownish-white cobaltous cyanide, $Co(CN)_2$, soluble in HCl, not in acetic acid or HCN, soluble in excess of the reagent:[3] $CoCl_2 + 2\,NaCN = Co(CN)_2 + 2\,NaCl$; $Co(CN)_2 + 4\,NaCN = Na_4Co(CN)_6$. Dilute acids, without digestion, precipitate $Co(CN)_2$ from this solution (same as Ni): $Na_4Co(CN)_6 + 4\,HCl = Co(CN)_2 + 4\,NaCl + 4\,HCN$. If the solution, containing excess of the alkali cyanide and a drop or two of acid (HCl), be digested hot for some time, the Co^{++} is oxidized to green cobalticyanide, $Co(CN)_6^{-3}$, corresponding to ferricyanide, but having no similar nickel compound: $4\,Co(CN)_6^{-4} + 4\,H^+ + O_2 = 4\,Co(CN)_6^{-3} + 2\,H_2O$. From the cobalticyanide solution, acids cause no precipitation (important distinction from Ni, whose solutions remain $Na_2Ni(CN)_4$ and, after digestion as above, form a precipitate with acids). The $Co(CN)_6^{-3}$, after removal of the Ni, can be precipitated with mercurous mercury. The oxidation of the Co may be hastened by addition of oxidizing agents as ClO^-, $Cr_2O_7^{--}$, etc. If Co^{++} is precipitated as $Co(OH)_2$ with a slight excess of NaOH, and the precipitate dissolved in the minimum amount of CN^-, addition of an oxidizing agent (ClO^-, $S_2O_8^{--}$, H_2O_2) to the cold solution causes no precipitation (important dis-

[1] See references to cobalt ammines, p. 332, footnote 2.

[2] Durrant, *Ch. News*, **73**, 228 (1896); Palit, *Ibid.*, **128**, 293 (1924); cf. Bernard and Job, *Compt. rend.*, **190**, 186–7 (1930), *C.A.* **24**, 2960.

[3] For a discussion of the complex cyanides of Co and Ni, see: Rossi, *Gazz. ch. ital.*, **45**, I, 6–10 (1915).

tinction from Ni); boiling completely precipitates $Co(OH)_3$. Both cobalto- and cobalti-cyanides form characteristic, insoluble precipitates with many of the heavy metals.

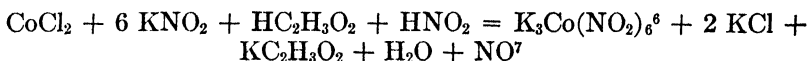
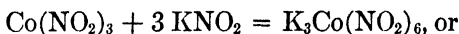
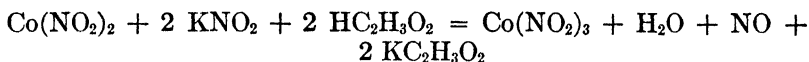
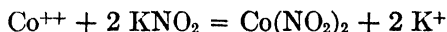
Ferrocyanides, as $K_4Fe(CN)_6$, precipitate cobaltous ferrocyanide, $Co_2Fe(CN)_6$, gray green, insoluble in acids. Ferricyanides, as $K_3Fe(CN)_6$, precipitate cobaltous ferricyanide, $Co_3[Fe(CN)_6]_2$, brownish red, insoluble in acids. A fairly distinctive test[1] for Co^{++} is obtained by adding $K_4Fe(CN)_6$ to the ammoniacal solution, whereupon a blood-red color (and precipitate, if sufficient Co is present) appears (distinction from Ni).[2] Thiocyanates in concentrated solution (30% or stronger),[3] give a blue solution with Co^{++}. Upon addition of amyl alcohol, the $Co(CNS)_4^{--}$ is concentrated in the upper, alcohol layer, and imparts a blue color to it (Vogel's reaction) (distinction from Ni). The test is very delicate. Its sensitivity is increased by using acetone instead of amyl alcohol.[4] Ferric ion interferes,[5] in that the red color of ferric thiocyanate masks the blue of the $Co(CNS)_4^{--}$. Reduction of the Fe^{+3} with $SnCl_2$ or precipitation with Na_2CO_3 will eliminate the difficulty. Mercuric salts and acetates also interfere to some extent.

c. Potassium nitrite added to a neutral or acetic acid solution of Co^{++} saturated with KCl, quickly forms a golden-yellow precipitate of potassium cobaltinitrite, $K_3Co(NO_2)_6$ (Fischer's salt). Shaking hastens precipitation, which is practically complete in about ten minutes (separation from Ni):

$$Co^{++} + 2\ KNO_2 = Co(NO_2)_2 + 2\ K^+$$

$$Co(NO_2)_2 + 2\ KNO_2 + 2\ HC_2H_3O_2 = Co(NO_2)_3 + H_2O + NO + 2\ KC_2H_3O_2$$

$$Co(NO_2)_3 + 3\ KNO_2 = K_3Co(NO_2)_6, \text{ or}$$

$$CoCl_2 + 6\ KNO_2 + HC_2H_3O_2 + HNO_2 = K_3Co(NO_2)_6{}^{[6]} + 2\ KCl + KC_2H_3O_2 + H_2O + NO^{[7]}$$

d. Phosphates, e.g., Na_2HPO_4, precipitate Co^{++} as red cobaltous phosphate, $CoHPO_4$; soluble in acids and NH_4OH. Sodium pyrophosphate forms a gelatinous precipitate with solutions of Co^{++}, soluble in excess of the reagent. The addition of $HC_2H_3O_2$ causes precipitation of the Co^{++}

[1] Grossmann, *Ch. Ztg.*, **31**, 37–8 (1907), states that other tests are better.
[2] Cf. Mindalev, *C.A.* **21**, 874 (1927).
[3] It is best to add a few crystals of the solid salt.
[4] Ditz, *Ch. Ztg.*, **46**, 121 (1922).
[5] Dorrington and Ward, *Analyst*, **54**, 327–32 (1929), *C.A.* **23**, 4637, suggest the use of KCNO to avoid interference of Fe^{+3}.
[6] Cf. §205, 6, *c*.
[7] Regarding change of $Co(NO_2)_2$ to $Co(NO_2)_3$, and for a review of the literature, see: Suzuki, *J. Ch. Soc.*, **97**, 726–32 (1910).

even in presence of tartrates (separation from Ni, but not from Fe or Mn).[1] If Co^{++} is treated with a saturated solution of ammonium phosphate, and the precipitate dissolved in HCl, when heated the addition of an excess of NH_4OH produces a blue precipitate of $CoNH_4PO_4$ (separation from Ni).

e. Hydrosulfic acid gradually and incompletely precipitates black cobaltous sulfide, CoS, from solutions of Co^{++}; from acetate solution the separation is fairly prompt and complete, but in presence of mineral acids, as in the second group, no precipitate forms. If, however, the cobalt is in NH_4OH solution, then the reaction is rapid and complete. When formed, the precipitate is at first distinctly soluble in dilute HCl, but upon standing 10 to 15 minutes, quite insoluble;[2] readily soluble in HNO_3 and even more easily in aqua regia. Upon exposure to the air, freshly precipitated CoS is gradually oxidized to the sulfate, as occurs with FeS. Alkali sulfides immediately and completely precipitate CoS, which is insoluble in excess of the reagent. Ammonium thioacetate precipitates CoS from ammoniacal solutions of Co^{++}. When Co^{++} is boiled with $Na_2S_2O_3$ in neutral solution, partial precipitation of CoS takes place.

f. The higher oxides of Co, also Co^{+3}, are reduced by warming with halogen acids, liberating the corresponding halogen (HCl does not reduce the Co in $Co(CN)_6^{-3}$ or in $Co(NH_3)_5Cl_3$). $CoCl_2$ in dilute aqueous solution is red; addition of concentrated HCl changes the color to blue (see above). This change will serve to detect 0.05 mg. of Co. Ni and Fe interfere, in that they give a green and yellow color, respectively; Mn^{++} does not interfere. If NaClO is added to a slightly acid Co^{++} solution, a precipitate of $Co(OH)_3$ forms in a short time. When an excess of alkali is present, the dark brown precipitate quickly formed contains more oxygen than corresponds to the formula $Co(OH)_3$.[3]

g. Soluble arsenites and arsenates precipitate Co^{++}, forming the corresponding cobalt arsenite or arserate, bluish white, soluble in NH_4OH or in acids, including arsenic acid.

h. Soluble chromates precipitate basic cobaltous chromate, reddish brown, from a neutral solution containing 0.0432 g. Co^{++} or more. The product is soluble in NH_4OH or in acids. No precipitate is obtained with $Cr_2O_7^{--}$.

i. $KMnO_4$, added to an NH_4OH solution of Co^{++}, oxidizes the Co^{++} to Co^{+3}, and prevents its precipitation by NaOH (separation from Ni).

j. Co^{++} in NH_4OH solution, warmed with H_2O_2 and then rendered acid with $HC_2H_3O_2$, is precipitated by $(NH_4)_2MoO_4$. Excess of the reagent in the filtrate does not interfere with the dioxime test for Ni.[4]

[1] Vortmann, *Ber.*, **21**, 1103 (1888).
[2] This may be due to polymerization of the CoS molecules. See under NiS, §133, 6, *e*.
[3] Howell, *J. Ch. Soc.*, **123**, 65 (1923).
[4] Carnot, *Compt. rend.*, **164**, 897 (1917).

7. Ignition. — In the bead of borax, and in that of microcosmic salt, with oxidizing and with reducing flames, cobalt gives an intense blue color. The blue bead of copper changes to brown in the reducing flame. If strongly saturated, the bead may appear black from intensity of color, but will give a blue powder. This important test is more delicate with the borax bead. Manganese, copper, nickel, or iron interfere somewhat. By ignition, with sodium carbonate on charcoal or with the reducing flame, compounds of cobalt are reduced to the metal (magnetic). Cobaltous oxide dissolves in melted glass and in other vitreous substances, coloring the mass blue. The black cobalto-cobaltic oxide, Co_3O_4, as left by ignition of cobaltous oxide or nitrate, combines or mixes, by ignition, with zinc oxide from zinc compounds to form a green, with aluminum compounds a blue, and with magnesium compounds a pink mass.

8. Detection. — After removal of the first three groups, cobalt is precipitated by H_2S in ammoniacal solution with Ni, Mn and Zn. The sulfides are digested with cold, 1 *N* HCl, which dissolves the MnS and ZnS (also traces of CoS and NiS). The residue is dissolved in aqua regia and the Co^{++} detected (*a*) by means of tests applicable in the presence of Ni, e.g., Vogel's reaction (6, *b*), the $NaHCO_3 + H_2O_2$ test (6, *a*), the cobaltinitrite test (6, *c*), etc. (*b*) *Organic reagents.* — (1) α-nitroso-β-naphthol completely precipitates Cu, Fe and Co; partially precipitates Ag, Sn and Bi; does not affect Pb, Hg, As, Sb, Cd, Al, Cr, Mn, Ni, Zn, Ca, Mg, or Be. The separation of Co from Ni is effected by adding the reagent[1] to a hot, acetic acid solution of Co^{++}. A voluminous precipitate of dark red cobalti-nitroso-β-naphthol, $[C_{10}H_6O(NO)]_3Co$, soon separates, which may be filtered and washed with 12% HCl (to remove Ni). Since the separation is quantitative, the precipitate may be ignited and weighed. This test is said to be more delicate than the cobaltinitrite reaction. (2) β-nitroso-α-naphthol, used in place of the alpha salt, is a more sensitive reagent[2] since it will detect as little as 1 mg. of Co^{++} in seventeen liters of solution. It produces a pale rose color. (3) If a slightly acid solution of Co^{++} is treated with 10% $NaC_2H_3O_2$ and diacetyldioxime (dimethylglyoxime), the solution becomes wine red upon addition of an alkaline sulfide.[3] (4) Potassium xanthate forms a green precipitate in neutral or slightly acid solutions of cobalt salts. Ni is also precipitated but dissolves in NH_4OH to give a blue solution.[4] (5) Nitroso-R-salt,[5] is added to a Co^{++} solution containing $NaC_2H_3O_2$. After heating to boiling, a little HNO_2 causes the development of a permanent red color [probably $(C_{10}H_5NO_8S_2Na_2)_3Co$]. Fe^{++} gives a green and Ni^{++} a brownish product.[6] (6) A 10% resorcinol solution

[1] Ilinski and Knorre, *Ber.*, **18**, 699 (1885): 4 g. in 150 cc. cold glacial acetic acid followed by dilution with an equal volume of water. Atack, *J. Soc. Ch. Ind.*, **34**, 641 (1915), claims that the Na salt is more stable and will readily detect one part of Co in a million parts of solution.

[2] Bellucci, *Gazz. ch. ital.*, **49**, II, 294–8 (1919).

[3] Matsui and Nakazawa, *Mem. Coll. Sci. Kyoto Imp. Univ.*, **4**, 265 (1920), *C.A.* **15**, 813. Cf. Braley and Hobart, *J. Am. Ch. Soc.*, **43**, 482 (1921).

[4] Compin, *Ann. ch. anal. ch. appl.*, **2**, ii, 218 (1920).

[5] 0.5 g. nitroso-R-salt in 100 cc. H_2O.

[6] van Klooster, *J. Am. Ch. Soc.*, **43**, 746 (1921).

added to an ammoniacal Co^{++} solution, gives, after heating a few minutes, a red to blue-violet color. Acidification changes the color to red.[1]

In addition to the reagents mentioned, many other organic compounds have been suggested for the detection of cobalt, e.g., glyoxaline;[2] catechol;[3] benzidine;[4] potassium dithio-oxalate.[5, 6]

9. Determination.[7] — *a. Gravimetrically,* Co may be precipitated and weighed as the cobaltinitrite, $K_3Co(NO_2)_6{\cdot}3H_2O$. The sulfide or oxide may be converted to the sulfate, ignited at 550°, and weighed as $CoSO_4$. Except where the amount of Co is small, precipitation with α-nitroso-β-naphthol, and after ignition, weighing as Co_3O_4, is unsatisfactory because of the uncertain composition of the oxide. This product may, however, be reduced to the metal in hydrogen, converted to the sulfate, or dissolved and deposited electrolytically.

b. Although many *volumetric* methods have been proposed, apparently the only accurate ones are those in which the Co^{++} is oxidized to Co^{+3}, the excess oxidizing agent removed, and the Co^{+3} titrated with a suitable reducing agent, e.g., addition of KI liberates I_2, which may be determined with thiosulfate.

c. Electrolytic methods involve, first, separation of Co^{++} from other metals,[8] and then deposition from ammoniacal solution. In case Ni has not been removed, the deposit of Co + Ni, after weighing, is dissolved, the Ni separated with diacetyldioxime and determined. Then the Co can be obtained by difference.

10. Oxidation and Reduction. — Co^{++} is oxidized to Co^{+3} in neutral or alkaline solution by PbO_2, ClO^-, BrO^-, I_2 and H_2O_2; in presence of acetic acid by KNO_2 (cf. 6, *c*). Co^{+3} is reduced to Co^{++} by $H_2C_2O_4$, H_3PO_2, H_2S, H_2SO_3, HCl, HBr, or HI. Metallic cobalt is precipitated from solutions of Co^{++} by Zn, Cd and Mg, etc.

§133. Nickel (German *nikker* = devil). Ni = 58.69. Atomic No. 28. Valence 2 or 3. Discovered by Cronstedt in 1751.

1. Physical Properties. — Density, 9.04 ± 0.03;[9] melting point, 1452°.[10] Nickel is a hard, silvery white metal, capable of taking a high polish. It is malleable,[11] ductile and very tenacious, forming wire stronger than iron but not quite as strong as cobalt (cf. §132, 1). Nickel is harder than pure iron but it does not oxidize in dry or moist air at ordinary temperatures. It is magnetic but loses its magnetism when heated above 345°. It burns with incandescence when heated in O, Cl, Br, or S. It becomes passive (like Fe) when dipped in concentrated HNO_3. Finely divided nickel will dissolve 17 times its own volume of hydrogen, hence finds extensive application in the hydrogenation of oils, etc.

[1] Lavoye, *J. Pharm. Belg.*, **3**, 889 (1921).

[2] Fischer, *Wiss. Veröffentlich. Siemens-Konzern*, **4**, 171 (1925), *B. C. A.* **1926**, 492.

[3] Weinland and Döttinger, *Z. anorg. allgem. Ch.*, **102**, 223 (1918), *C.A.* **12**, 2503.

[4] Feigl, *Ch. Ztg.*, **44**, 689 (1920).

[5] Jones and Tasker, *J. Ch. Soc.*, **95**, 1904 (1909).

[6] Gutzeit, *Helv. Ch. Acta*, **12**, 713–40 (1929), *C.A.* **23**, 4644, has considered a number of tests for Co.

[7] See: Margosches, Vol. 16.

[8] See Willard and Hall, *J. Am. Ch. Soc.*, **44**, 2219 (1922).

[9] Davey, *Phys. Rev.*, [2] **25**, 753 (1925); cf. Thomson, *Nature*, **123**, 912 (1929), who gives 8.86 as the density of Ni.

[10] B. Stds. Cir. 35; Wensel and Roeser, *B. Stds. J. Research*, **5**, 1309–18 (1930), report 1455° ± 1° as the freezing point of 99.94% pure Ni.

[11] Traces of oxide make it brittle.

It is much used in electroplating other metals, both for ornamental purposes and to inhibit corrosion, and in making coins of small denominations (Ni, 25%; Cu, 75%). Nickel steel containing about 5% Ni is extensively used. Chrome-nickel steel, containing about 1% Cr and 3% Ni, accounts for about 30% of the Ni annually produced. "Invar," a Ni-Fe alloy containing 36% Ni, has a very low coefficient of expansion, hence is used for the highest grade secondary standards of length, etc. "Permalloy" (80% Ni–20% Fe) is used as a sheathing for electric cables. Its magnetic permeability is 200 times that of pure iron. Monel metal is a "natural" alloy,[1] containing two parts Ni to one part Cu (and 2%–4% Fe + Mn). Nichrome wire (11%–25% Cr, up to 25% Fe, balance Ni) is extensively used in making heating elements for electric stoves, etc.; German, or nickel, silver is 50%–65% Cu, 10%–30% Ni, and the balance Zn. Nickel is also used in the Edison or alkaline storage battery.

2. Occurrence. — There are two commercial sources of nickel. The principal one is the Sudbury district in the province of Ontario, Canada; the other is the island of New Caledonia, in the southern Pacific Ocean. The Sudbury ore is pentlandite, $NiS \cdot 2FeS$, mixed with pyrrhotite and chalcopyrite, and containing on the average, 3% Ni and 1.5% Cu, along with some Fe and precious metals. The New Caledonia deposit is a silicate, nickeliferous serpentine, carrying 4%–8% Ni but no Cu. In 1928 the Sudbury district produced about 48,000 tons of Ni, which was 90% of the world's production. The present (1931) wholesale price of nickel is about 35 cents a pound.

3. Preparation.[2] — The ore is roasted in heaps in the open air (cf. §132, 3) to reduce the sulfur content. The product is smelted and a matte obtained, containing about 25% Cu plus Ni. After treatment in a Bessemer converter, the resulting matte contains 56% Ni, 24% Cu and 20% S. Refining is effected by (1) the Hybinette or electrolytic process, in which much of the Cu is first leached out then the residue is melted and made into anodes, from which the Ni is removed electrolytically; (2) the Mond process, which involves roasting the matte to form NiO, slightly soluble, and CuO (possibly some basic $CuSO_4$), readily soluble in dilute acid. Removal of the Cu by leaching with dilute H_2SO_4 is followed by reduction with H_2 and action of CO on the residual metallic Ni at 50°. The nickel carbonyl, $Ni(CO)_4$, thus formed (a very poisonous gas) is decomposed in a chamber of Ni shot at 200°. The Ni deposits on the shot and the CO passes off to be used again; (3) the Orford process, which is rapidly being displaced.

4. Oxides and Hydroxides. — Nickelous oxide, NiO, is formed when the carbonate, nitrate or hydroxide is strongly ignited. It is green to gray green when cold, yellow when hot. Nickelous hydroxide, $Ni(OH)_2$, light green, is formed by treatment of Ni^{++} with a fixed alkali hydroxide. The existence of nickel sesquioxide, Ni_2O_3, is questioned by some authorities.[3] It is claimed that treatment of Ni^{++} with a fixed alkali and an oxidizing agent, e.g., ClO^-, gives the hydrated dioxide, $NiO_2 \cdot H_2O$ (possibly peroxide), although by analogy one would expect both Ni_2O_3 and Ni_3O_4 to be formed.[4]

5. Solubilities. — *a. Metal.* — HCl or H_2SO_4, dilute or concentrated, attacks Ni° but slowly; dilute HNO_3 dissolves it readily, but in the concentrated acid passivity ensues. Ni° is not readily attacked when heated in contact with the alkali hydroxides or carbonates, hence the use of Ni crucibles for caustic fusions.

b. Oxides and Hydroxides. — Nickelous oxide and hydroxide are insoluble in water[5] or fixed alkalis, soluble in acids or NH_4OH. The higher oxides (see 4, above), are dissolved by acids with reduction to Ni^{++} and, in case a halogen acid is involved, liberation of the halogen; with dilute H_2SO_4 oxygen is evolved.

c. Salts. — The salts of Ni have a pale green color in crystals and in solution; when anhydrous, they are yellow. The nitrate and chloride are deliquescent or efflorescent, according to atmospheric conditions; the

[1] Made directly from the ore.

[2] Cf. Evans, III, p. 181.

[3] E.g., Hendricks, *et al.*, *Z. Krist.*, **73**, 376–80 (1930), *C.A.* **24**, 4438.

[4] Friend, IX, 1, p. 117; Howell, *J. Ch. Soc.*, **123**, 669–76, 1772–83 (1923); Latimer and Hildebrand, p. 322–3.

[5] Almkvist, *Z. anorg. allgem. Ch.*, **103**, 240 (1918), states that the solubility of $Ni(OH)_2$ in H_2O is 12.7 mg./l. at 20°.

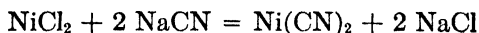
acetate is efflorescent. The chloride vaporizes at high temperatures. A solution containing 3 Ni^{++} to 1 Co^{++} is colorless.

The carbonate, sulfide, phosphate, borate, oxalate, cyanide, ferrocyanide and ferricyanide are insoluble; the double cyanide of Ni and an alkali metal is soluble in water. The chloride is soluble in alcohol and the nitrate in dilute alcohol. Many salts of Ni form soluble compounds with NH_4OH.

6. Reactions. — *a.* Alkali hydroxides precipitate[1] from Ni^{++} solutions, nickelous hydroxide, $Ni(OH)_2$, pale green; not oxidized upon exposure to the air (§132, 6, *a*); oxidized by BrO^-, ClO^-, $Fe(CN)_6^{-3}$ or $S_2O_8^{--}$, but not by dilute H_2O_2 or I_2 (distinction from Co^{++}). Nickelous hydroxide is insoluble in excess of NaOH, soluble in NH_4OH or ammonium salts, forming a greenish-blue to violet-blue solution of $Ni(NH_3)_6^{++}$. Ammonium hydroxide in small amount precipitates $Ni(OH)_2$ from solutions of Ni^{++}, soluble in excess to give $Ni(NH_3)_4^{++}$ or $Ni(NH_3)_6^{++}$, reddish blue. No precipitate is formed if an ammonium salt is present. Excess of fixed alkali hydroxide will slowly precipitate $Ni(OH)_2$ from ammoniacal solutions (distinction from Co). Nickel-ammonia bromide, $Ni(NH_3)_6Br_2$, purple, is precipitated upon addition of concentrated NH_4OH to a hot solution of $NiBr_2$ (separation from Co if present as the ammine). The iodide formed in a similar way is less soluble than the bromide.[2] Alkali carbonates precipitate from Ni^{++} solutions a green, basic carbonate; the normal carbonate, $NiCO_3 \cdot 6H_2O$, is obtained if an excess of carbonic acid is present. The precipitate separating upon addition of $(NH_4)_2CO_3$ to a solution of Ni^{++}, dissolves in excess of the reagent. Carbonates of Ba, Sr, Ca and Mg are without action on Ni^{++} in the cold (distinction from Fe^{+3}, Al^{+3} and Cr^{+3}), but on boiling, completely precipitate the Ni.

b. Oxalic acid and soluble oxalates precipitate nickel oxalate which is green. The separation takes place slowly being almost complete after about twenty-four hours. Alkali cyanides precipitate nickel cyanide, $Ni(CN)_2$, yellowish green, insoluble in cold, dilute HCl; readily soluble in excess of the reagent, forming the complex $Ni(CN)_4^{--}$:[3]

$$NiCl_2 + 2\ NaCN = Ni(CN)_2 + 2\ NaCl$$

$$Ni(CN)_2 + 2\ NaCN = Na_2Ni(CN)_4$$

Careful addition of acid to $Ni(CN)_4^{--}$ precipitates $Ni(CN)_2$. Furthermore, $Ni(CN)_4^{--}$ cannot be oxidized to the nickelic compound (distinction from Fe^{++} and Co^{++}). If to a solution of $Ni(CN)_4^{--}$ are added NaOH and Br_2, Cl_2 or ClO^-, a brown precipitate is obtained (distinction from Co).

[1] The presence of non-volatile organic acids inhibits or prevents precipitation.
[2] Agrestini, *Gazz. ch. ital.*, **48**, II, 30 (1918).
[3] Rossi, *Gazz. ch. ital.*, **45**, I, 6-10 (1915), *C.A.* **9**, 1438.

The test is affected by the excess of cyanide[1] present, in that a large amount of oxidizing agent must be used when too much has been added, whereupon, due to dilution, only a brown coloration will be obtained. Ferrocyanides precipitate a greenish-white nickel ferrocyanide, $Ni_2Fe(CN)_6$,[2] insoluble in acids, soluble in NH_4OH, decomposed by the fixed alkalis. Ferricyanides precipitate greenish-yellow nickel ferricyanide, $Ni_3[Fe(CN)_6]_2$, insoluble in acids, soluble in NH_4OH to give a green solution (§132, 6, *b*). Ni^{++} is not visibly affected by CNS^- (distinction from Co).

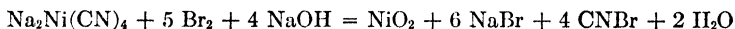
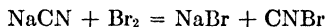
c. Potassium nitrite, in presence of acetic acid, does not oxidize Ni^{++} (distinction from Co).

d. Sodium phosphate, Na_2HPO_4, precipitates green nickel phosphate, $Ni_3(PO_4)_2$, soluble in acids, including acetic.

e. Hydrosulfic acid precipitates from neutral solutions of nickel salts, a part of the Ni as NiS, black. Precipitation takes place slowly, and, from a solution containing sufficient acetate ion, is complete. In the presence of mineral acids, i.e., high $[H^+]$, no precipitation takes place. Alkali sulfides precipitate the whole of the Ni as the black sulfide. Although precipitation is prevented by high $[H^+]$, the precipitate, once formed, is quite insoluble in dilute hydrochloric acid, slowly soluble in concentrated HCl, readily in HNO_3 and aqua regia. Thiel and Gessner[3] explain this insolubility of NiS by assuming that the sulfide formed initially is αNiS. After a short time this changes to βNiS, which soon becomes γNiS. The first and second forms are soluble in cold and hot HCl, respectively, while the γ form is quite insoluble. These forms may result from polymerization, $x\text{NiS} \rightarrow (\text{NiS})_x$.[4] NiS is partially soluble (or peptized)[5] in $(NH_4)_2S_x$, from which brown-colored system it is precipitated on addition of acetic acid and boiling (distinction from Co). Freshly precipitated NiS is soluble in KCN; addition of HCl or H_2SO_4 causes precipitation of $Ni(CN)_2$ (separation from Co). When Ni^{++} is boiled with a thiosulfate, a portion of the Ni^{++} is precipitated as NiS. If a nitrite is added along with the thiosulfate, a permanganate-colored liquid is obtained, from which dark purple crystals soon separate[6] (distinction from large amounts of Co).

[1] The bromine oxidizes this to cyanogen bromide, CNBr, before attacking the complex cyanide.

$$NaCN + Br_2 = NaBr + CNBr$$

$$Na_2Ni(CN)_4 + 5\ Br_2 + 4\ NaOH = NiO_2 + 6\ NaBr + 4\ CNBr + 2\ H_2O$$

If insufficient oxidizing agent is added to exceed the cyanide used the test will fail even though Ni is present.

[2] Werner, *Pharm. Ztg.*, **55**, 211–2 (1910).

[3] Thiel and Gessner, *Z. anorg. allgem. Ch.*, **86**, 1–57 (1914).

[4] Cf. Gluud and Schönfelder, *Ber.*, **57B**, 628–9 (1924); Ephraim, *Ibid.*, **56B**, 1885–6 (1923).

[5] Cf. Thorne and Pates, *Kolloid Z.*, **38**, 155–8 (1926).

[6] Ball, *J. Ch. Soc.* (*Proc.*), **26**, 329 (1910).

f. The halogen acids reduce the higher oxide of Ni to Ni^{++} with liberation of the corresponding halogen. Potassium iodide added to freshly precipitated nickel peroxide (see 4, above), gives I_2 (distinction from Co). $Ni(NH_3)_6^{++}$ treated with NH_4ClO_4, gives a precipitate of $Ni(NH_3)_6(ClO_4)_2$, clear blue. $Co(NH_3)_6^{++}$ gives a yellowish-red precipitate, but not if boiled with H_2O_2 before addition of the perchlorate (separation of Ni from Co).

g. Ni^{++} is precipitated by AsO_3^{-3} or AsO_4^{-3}, white or greenish white, soluble in acids.

h. Chromates precipitate from neutral solutions of Ni a yellow to brown basic chromate, $NiCrO_4 \cdot 2NiO$, soluble in acids.[1] $K_2Cr_2O_7$ forms no precipitate. A saturated solution of $(NH_4)_2MoO_4$ slowly forms, in neutral or slightly acid solutions of Ni^{++} at about 70°, a greenish-white precipitate (distinction from Co).[2]

7. **Ignition.**[3] — Nickel compounds dissolve clear in the borax bead, giving with the oxidizing flame a purple-red or violet color while hot, becoming yellowish brown when cold; with the reducing flame, fading to a turbid gray, from reduced metallic nickel, and finally becoming colorless. The addition of any potassium salt, as potassium nitrate, causes the borax bead to assume a dark purple or blue color, clearest in the oxidizing flame. With microcosmic salt, nickel gives a reddish-brown bead, cooling to a pale reddish yellow, the colors being alike in both flames. Hence, with this reagent, in the reducing flame, the color of nickel may be recognized in presence of iron and manganese, which are colorless in the reducing flame; but cobalt effectually obscures the bead test for nickel. The yellow red of copper in the reducing flame, persisting in beads of microcosmic salt, also masks the bead test for nickel. By ignition with sodium carbonate on charcoal, compounds of nickel are reduced to the metal, slightly attracted by the magnet.

8. **Detection.** — After removal of Group III, H_2S is passed into the ammoniacal filtrate, thus precipitating NiS along with CoS, MnS and ZnS. Filtration is delayed somewhat, permitting NiS to change to the γ form. Then the precipitate is digested with cold 1 N HCl. The residue of NiS and CoS is dissolved in HNO_3 or aqua regia and the Ni^{++} detected in the presence of Co^{++} or after its removal (§132, 8).

a. (1) Ni^{++}, precipitated as $Ni(CN)_2$ and dissolved in a slight excess of CN^-, gives, when treated with a few drops of NaOH and sufficient Br_2 or NaClO, a brown to black precipitate. (2) Ni^{++} is treated with NH_4Cl and excess NH_4OH. Addition of a persulfate to the hot solution oxidizes any cobalt to form a red cobaltiammine. (There should be no precipitate at this stage.) After removal of any large excess of NH_4OH by boiling, the solution is cooled. Upon addition of NaOH and shaking, dark brown

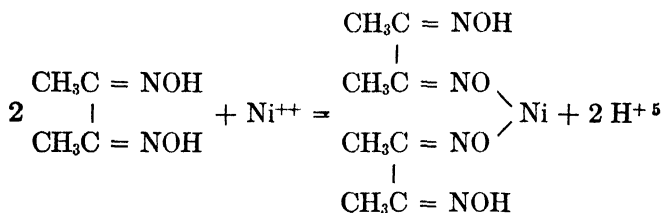
[1] Weil, *Bull. soc. ch.*, [4] **9**, 20–2 (1911), *C.A.* **5**, 1376.

[2] Pozzi-Escot, *Compt. rend.*, **145**, 435 (1907), *C.A.* **2**, 1666.

[3] Curtman and Rothberg, *J. Am. Ch. Soc.*, **33**, 188–9 (1911), consider the efficiency of borax bead tests for Ni and Co.

to black NiO_2 (see 4) slowly precipitates. If Co is present the filtrate will be pink to red.[1, 2]

b. Undoubtedly the most widely used test for Ni^{++} depends upon the fact that various dioximes form characteristic red precipitates in ammoniacal or buffered acetic acid solutions. (1) Dimethylglyoxime[3] (better diacetyldioxime), will detect one part of Ni in 400,000[4] of solution. Co gives no precipitate but interferes if present in large excess, i.e., more than 10 Co : 1 Ni. Fe^{++} gives a red color but no precipitate (§126, 8).

$$2\begin{matrix} CH_3C = NOH \\ | \\ CH_3C = NOH \end{matrix} + Ni^{++} = \begin{matrix} CH_3C = NOH \\ | \\ CH_3C = NO \diagdown \\ \qquad\quad Ni \\ CH_3C = NO \diagup \\ | \\ CH_3C = NOH \end{matrix} + 2\,H^{+}\ [5]$$

(2) Alpha-benzildioxime,[6] while a more sensitive reagent, is not extensively used because of its low solubility. (Probably this objection could be overcome by substituting a sulfonic acid group in the ring.) The results

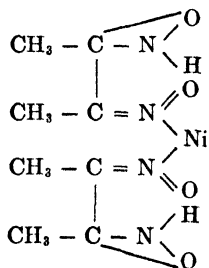
[1] No Co is precipitated unless the solution is warm. The amount of NaOH required to precipitate the Ni depends upon the excess of NH_4OH and NH_4Cl present.

[2] Pozzi-Escot, *loc. cit.*, claims that ammonium molybdate is a satisfactory reagent for Ni^{++}. Others disagree.

[3] Tschugaeff, *Ber.*, **38**, 2520 (1905).

[4] Cf. Feigl, *Ber.*, **57B**, 758–61 (1924), who claims that by his procedure the test is four times as delicate; Chapman, *J. Ch. Soc.* (*Trans.*), **111**, 213 (1917), who claims a delicacy of 1 : 30,000,000. Middleton and Miller, *J. Am. Ch. Soc.*, **38**, 1705–11 (1916), add the dioxime to a cyanide solution of Ni and Co, then replace the Ni with Ag. The method is suggested for detection of Ni in Co salts.

[5] Barker, *Ch. News*, **130**, 99–100 (1925), gives

$$\begin{matrix} CH_3 - C - N \diagup O \\ \quad | \qquad \diagdown H \\ \quad | \qquad \diagup\!\!\diagup O \\ CH_3 - C = N \\ \qquad\qquad \diagdown Ni \\ \qquad\qquad \diagup \\ CH_3 - C = N \\ \quad | \qquad \diagdown\!\!\diagdown O \\ \quad | \qquad \diagup H \\ CH_3 - C - N \diagdown O \end{matrix}$$

Cf. Matsui, *J. Tokyo Ch. Soc.*, **39**, 459 (1918), *C.A.* **12**, 2292; Pfeiffer, *Ber.* **61B**, 103 (1928); Thilo and Friedrich, *Ber.*, **62B**, 2990–3000 (1929), *C.A.* **24**, 1309.

[6] Atack, *Analyst*, **38**, 316 (1913); *Z. anal. Ch.*, **53**, 620 (1914).

and procedure are the same as in (1). (3) Dicyandiamidine sulfate[1, 2] gives, with $Ni(NH_3)_6^{++}$ in the presence of a small amount of ammonium salts and a large excess of NH_4OH, a crystalline, yellow precipitate. Cobalt delays precipitation and gives a red color to the solution. (4) A solution of potassium xanthate[3] precipitates Ni^{++} (and Co^{++}) from neutral solution. The precipitate is soluble in NH_4OH (distinction from Co), and reprecipitated by $(NH_4)_2S$.[4] The xanthate also precipitates Ni in alkaline solution in presence of $Na_4P_2O_7$ (separation from Fe^{+3}).[5] (5) Potassium dithio-oxalate[6] gives a deep magenta color with Ni^{++}. The test is very delicate.[7]

9. Determination.[8] — *Gravimetrically,* nickel may be precipitated as the dioxime, (a) dried at 120°, then weighed, (b) ignited to NiO and weighed, (c) dissolved, and after destruction of the organic matter, electrolyzed in ammoniacal solution, thus obtaining a deposit of metallic Ni. *Volumetrically,* Ni may be determined by titration of the $Ni(NH_3)_6^{++}$ with standardized KCN, using AgI[9] or α-benzildioxime[10] as an internal indicator.

10. Oxidation and Reduction. — Ni^{++} is changed to $NiO_2 \cdot nH_2O$ in the presence of fixed alkalis by ClO^- or BrO^- but not by iodine (distinction from Co).[11] Nickel dioxide is reduced slowly, with evolution of oxygen, by all non-reducing acids; *without* evolution of O_2 by reducing acids, which are themselves oxidized: $H_2C_2O_4$ forms CO_2, HNO_2 becomes HNO_3,

[1] Grossmann and Schuck, *Ber.*, **39**, 3356 (1906); Grossmann and Heilborn, *Ibid.*, **41**, 1878 (1908).

[2] Dicyandiamidine is $NH_2 \cdot (NH:)\, C \cdot NH \cdot CONH_2$. The salt formed is $(C_2H_5N_4O)_2Ni \cdot 2H_2O$. See: Rüdisüle, V, p. 130.

[3] $C_2H_5O - C = S(-SK)$, prepared by the action of alcoholic potash on CS_2.

[4] Phipson, *Ch. News*, **36**, 150 (1877).

[5] Campbell and Andrews, *Am. Ch. J.*, **17**, 164 (1895).

[6] Jones and Tasker, *J. Ch. Soc.*, **95**, 1904 (1909).

[7] Other tests for Ni: Vincent, *Z. anal. Ch.*, **19**, 480 (1880), suggests dimethylamine, giving an apple-green precipitate.

Cerdan and Ferrer, *Anales soc. españ. fís. quím.*, **9**, 201, 272 (1911), *C.A.* **6**, 462, cf. *C.A.* **5**, 3392, suggest potassium methyl xanthogenate.

Lavoye, *J. pharm. de Belg.*, **3**, 889 (1921), *C.A.* **16**, 882, suggests a 10% resorcinol solution.

Malatesta and di Nola, *Boll. ch. farm.*, **52**, 819 (1913), *C.A.* **9**, 2200, suggest 1, 2-diaminoanthraquinone-3-sulfonic acid.

Ilinski and von Knorre, *Z. anal. Ch.*, **24**, 595 (1885), state that α-nitroso-β-naphthol in 50% $HC_2H_3O_2$ gives a brown precipitate, $[C_{10}H_6O(NO)]_2Ni$, decomposed by HCl and H_2SO_4, hence no interference with the test for Co.

Braun, *Z. anal. Ch.*, **7**, 346 (1868), suggested potassium thiocarbonate, K_2CS_3, which gives with $Ni(NH_3)_6^{++}$ a red-brown solution.

Gutzeit, *Helv. Ch. Acta*, **12**, 713–40 (1929), *C.A.* **23**, 4644, has described a number of other tests.

[8] For a discussion of the older methods, see: Margosches, Vol. 16.

[9] Campbell and Andrews, *J. Am. Ch. Soc.*, **17**, 127 (1985).

[10] Kelly and Conant, *Ind. Eng. Ch.*, **8**, 803 (1916).

[11] Donath, *Ber.*, **12**, 1868 (1879).

H_3PO_2 yields H_3PO_4, H_2S is oxidized to S, H_2SO_3 to H_2SO_4, HCl to Cl_2, HBr to Br_2, HI to I_2, HCNS to HCN and H_2SO_4, $H_4Fe(CN)_6$ to $H_3Fe(CN)_6$. Ni^{++} is reduced to the metal by finely divided Zn, Cd, or Sn.

§134. Manganese (L. *Magnes* = magnet). Mn = 54.93. Atomic No. 25. Valence 2, 3 (?), 4, 6 and 7. Discovered by Scheele in 1774.

1. Physical Properties. — Density, 7.03;[1] melting point, 1264° ± 10°[2] (sample was 97.3% Mn); boiling point, 1900°;[3] it volatilizes appreciably at temperatures but slightly above the melting point. Manganese is a brittle metal, having the general appearance of cast iron. It is non-magnetic, takes a high polish, is not very hard if pure, but small amounts of carbon harden it sufficiently to scratch steel. It is readily oxidized, decomposing water at but little above room temperature. It is used largely as ferromanganese in the manufacture of steel. Small quantities of Mn are added to steel for deoxidation; larger quantities (*ca.* 12%) produce a very tough " work hardening " alloy. Other uses, as MnO_2, are: in dry cells, for the manufacture of chlorine and bromine, as a dryer in paints and varnishes and to color glass and ceramic ware.

2. Occurrence. — Manganese is not found native. It is present in nearly all iron ores. Its chief source, however, is pyrolusite, MnO_2. It is also found as manganite, MnO(OH), rhodochrosite, $MnCO_3$, wolframite, $(FeMn)WO_4$, franklinite, (FeMnZn) $(FeO_2)_2$, and as a constituent of many other minerals. The ores are fairly widely distributed, the chief commercial deposits being in the Caucasus Mountains, the United States, India, Brazil, Spain, Egypt, the " Gold Coast " of Africa and Czechoslovakia. The total production of high grade ore in 1928 was close to 3 million tons, valued at $40–$80 per ton, depending on the manganese content.

3. Preparation. — Metallic manganese is not a commercial article. Since practically the whole output is consumed in the manufacture of steel, ferromanganese and spiegeleisen are the forms marketed. The former contains about 78% Mn and is chiefly consumed in the open hearth process. The latter contains 12%–33% Mn and is used in the Bessemer process. Both alloys are prepared in a blast furnace by the reduction of a mixture of iron and manganese ores. The metal itself may be obtained by reduction of one of its compounds with Na°, Mg°, C°, or Al° (thermite process).

4. Oxides and Hydroxides. — Oxides and hydroxides are found with Mn having valences of 2, 3 and 4; the salts exist most commonly as Mn^{++}, with some unstable Mn^{+3} and Mn^{+4} salts; as an anion it forms a manganate, MnO_4^{--}, and a permanganate, MnO_4^-. (a) Manganous oxide, MnO, is formed (1) by simple ignition of $Mn(OH)_2$, $MnCO_3$ or MnC_2O_4, air being excluded; (2) by ignition of any of the higher oxides of Mn with H_2 in a closed tube. If prepared at as low a temperature as practicable, it is a dark gray or greenish-gray powder, and oxidizes quickly in the air to Mn_3O_4. If prepared at a higher temperature, it is more stable. Manganous hydroxide, $Mn(OH)_2$, is formed from Mn^{++} salts by precipitation with alkalis. It quickly oxidizes in the air, forming $Mn(OH)_3$, MnO(OH) or (possibly), $MnO{\cdot}MnO_2{\cdot}nH_2O$, or perhaps a mixture of all three, thus changing from white to brown. (b) Manganic oxide,[4] Mn_2O_3, is obtained upon heating MnO_2 for 20 hours at 700°.[5] Manganic oxyhydroxide, MnO(OH) (see above), is formed by oxidation of $Mn(OH)_2$ in the air. (c) Trimanganese tetroxide, Mn_3O_4, is formed when any of the higher or lower oxides of Mn, or any Mn^{++} salt with a volatile acid, is heated at 1000° for 6–8 hours.[6] The corresponding hydroxide has

[1] Campbell, *J. Ch. Soc.*, **123**, 2323 (1923).

[2] Burgess and Waltenberg, *Z. anorg. allgem. Ch.*, **82**, 361 (1913).

[3] Greenwood, *Proc. Roy. Soc.* (London), **A82**, 396 (1909).

[4] Meyer and Kanters, *Z. anorg. allgem. Ch.*, **185**, 177–83 (1929). This is their seventh paper on the subject.

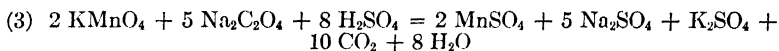
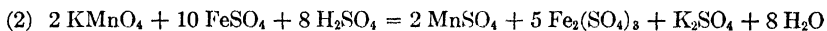
[5] Cf. Schneider, *Pogg. Ann.*, **107**, 605 (1859).

[6] Meyer and Kanters, *loc. cit.*

not been isolated. It is believed that Mn_3O_4 is a double oxide — $MnO \cdot Mn_2O_3$.[1] It decomposes in dilute acid solution: $Mn_3O_4 \rightarrow 2\ MnO + MnO_2$. (d) Manganese dioxide, MnO_2, is formed: (1) by heating $Mn(NO_3)_2$ to 200°; (2) by heating $MnCO_3$ with a chlorate to 300°; (3) by boiling any Mn^{++} salt with concentrated HNO_3 and a chlorate. The corresponding hydroxide, $Mn(OH)_4$, has not been isolated. Several other hydroxides have been reported, e.g., $MnO(OH)_2$, $Mn_2O_3(OH)_2$, etc. (e) Manganic acid, H_2MnO_4, is not known in the free state. Manganates, MnO_4^{--}, green, are formed when any compound of Mn is fused with (1) NaOH or Na_2CO_3 in air, oxygen being absorbed:[2] $2\ MnO_2 + 4\ NaOH + O_2 = 2\ Na_2MnO_4 + 2\ H_2O$; (2) $NaNO_3$ or $KClO_3$, NO or KCl being formed. (3) A manganate is readily obtained upon reduction of MnO_4^- in alkaline solution, with a small amount of KI. (f) Permanganic acid is not in use as an acid, but is represented by the permanganates, e.g., $KMnO_4$, reddish purple. A permanganate is at once decomposed by addition of hot H_2SO_4 to the solid salt (Eq. 1), but in aqueous solution decomposition does not at once take place, except by contact with reducing agents. The oxidizing power of MnO_4^- extends to a great number of substances; it varies in acid and in alkaline solutions, and acts in many cases so rapidly as to be violently explosive. In volumetric analysis, $KMnO_4$ is probably the most widely used oxidizing agent. The reactions with Fe^{++} (Eq. 2) and oxalate (Eq. 3) are especially important.

(1) $4\ KMnO_4 + 6\ H_2SO_4 = 4\ MnSO_4 + 2\ K_2SO_4 + 5\ O_2 + 6\ H_2O$

(2) $2\ KMnO_4 + 10\ FeSO_4 + 8\ H_2SO_4 = 2\ MnSO_4 + 5\ Fe_2(SO_4)_3 + K_2SO_4 + 8\ H_2O$

(3) $2\ KMnO_4 + 5\ Na_2C_2O_4 + 8\ H_2SO_4 = 2\ MnSO_4 + 5\ Na_2SO_4 + K_2SO_4 + 10\ CO_2 + 8\ H_2O$

5. Solubilities. — *a. Metal.* — Manganese reacts with warm water to give $Mn(OH)_2$ and H_2. It dissolves readily in dilute acids to form Mn^{++}. Concentrated H_2SO_4 dissolves it only on warming, SO_2 being evolved. It combines readily with Cl and Br.

b. Oxides and Hydroxides. — All oxides and hydroxides of Mn are insoluble in H_2O. They are soluble in warm HCl, forming Mn^{++}, the higher oxides and hydroxides being reduced with evolution of Cl_2. HBr and HI act similarly and more readily than HCl. (H_2SO_4 and a halide may be used in place of the acid itself.) In the cold, HCl dissolves MnO_2 to give a greenish-brown, unstable solution evolving Cl_2 when warmed and precipitating MnO_2 when diluted with much H_2O.[3] The acids HNO_3 and H_2SO_4 dissolve MnO and $Mn(OH)_2$ to form Mn^{++}. MnO_2 (or the hydrated oxide) is insoluble in HNO_3, dilute or concentrated, but the addition of a few drops of H_2O_2 causes rapid solution with the formation of Mn^{++}. Concentrated H_2SO_4, with heat, decomposes MnO_2, evolving O_2 and forming Mn^{++}: $2\ MnO_2 + 2\ H_2SO_4 = 2\ MnSO_4 + 2\ H_2O + O_2$. Manganous hydroxide is insoluble in the alkalis but soluble in solutions of ammonium salts.

c. Salts. — Manganous sulfide, carbonate, phosphate, oxalate, borate and sulfite are insoluble in H_2O, readily soluble in dilute acids. Mn^{+3} salts are somewhat unstable compounds, of a reddish-brown or purple-red color, becoming paler and of lighter tint on reduction to Mn^{++}. Manganous nitrate, chloride and sulfate are deliquescent. $MnCl_3$ exists only in solution; it is reduced to Mn^{++} by boiling and by evaporation to the solid. Manganic sulfate, $Mn_2(SO_4)_3$, is soluble in dilute H_2SO_4, but forms Mn^{++} if treated with H_2O alone; potassium manganic sulfate and other manganic alums are also decomposed by H_2O. Alkali manganates and permanganates are soluble in H_2O but the former rapidly decompose: $3\ MnO_4^{--} + 2\ H_2O \rightarrow 2\ MnO_4^- + MnO_2 + 4\ OH^-$. Free alkali retards,

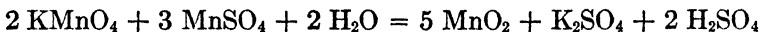
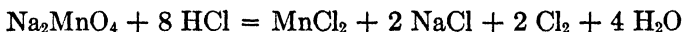
[1] Meyer and Kanters, *loc. cit.*

[2] Cf. Sackur, *Ber.*, **44**, 777–87 (1911), who gives as the product, $Mn_2O_5 \cdot 4Na_2O$.

[3] Cf. Holmes, *J. Am. Ch. Soc.*, **29**, 1277–88 (1907).

free acid and boiling promote, this change. In the presence of reducing agents, both MnO_4^{--} and MnO_4^- are reduced to lower forms:

$$Na_2MnO_4 + 8\ HCl = MnCl_2 + 2\ NaCl + 2\ Cl_2 + 4\ H_2O$$

$$2\ KMnO_4 + 3\ MnSO_4 + 2\ H_2O = 5\ MnO_2 + K_2SO_4 + 2\ H_2SO_4$$

6. Reactions. — *a.* The fixed alkali hydroxides precipitate,[1] from solutions of Mn^{++}, manganous hydroxide, $Mn(OH)_2$, white, soon turning brown in the air by oxidation to the manganic hydroxide, $Mn(OH)_3$: $4\ Mn(OH)_2 + O_2 + 2\ H_2O = 4\ Mn(OH)_3$; $2\ Mn(OH)_2 + O_2 = 2\ MnO_3H_2$ (cf. 4). The precipitate is insoluble in excess of the alkalis, but before oxidation is soluble in excess of ammonium salts. From solutions of Mn^{++}, NH_4OH precipitates the Mn incompletely as the hydroxide. If sufficient ammonium salt is initially present, no precipitate is obtained (separation of Mn from Group III), due to the common ion effect. However, on exposure to air, the Mn^{++} is readily oxidized to Mn^{+3}, whereupon brown manganic hydroxide is precipitated. Alkali carbonates precipitate manganous carbonate, $MnCO_3$, white, oxidized by the air to form manganic hydroxide. Before oxidation precipitation is incomplete if an ammonium salt is present. Concentrated NH_4OH gradually reduces MnO_4^- to MnO_2.

b. Manganous oxalate, MnC_2O_4, is obtained upon adding $C_2O_4^{--}$ to a solution of Mn^{++}. The precipitate is soluble in mineral acids not too dilute. All compounds of Mn of a higher degree of oxidation are reduced to Mn^{++} on warming with $C_2O_4^{--}$ in the presence of a mineral acid (see 4, Eq. 3).

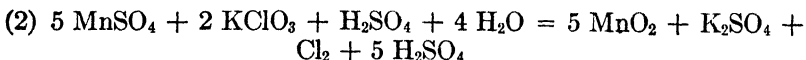
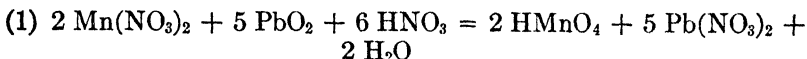
Soluble cyanides, as NaCN, precipitate manganous cyanide,[2] $Mn(CN)_2$, white, darkening in the air, soluble in excess of the reagent due to the formation of $Mn(CN)_6^{-4}$. This solution, exposed to the air, produces $Mn(CN)_6^{-3}$. Fe^{+3} and Mn^{++} may be separated by treating the two ions with an excess of CN^- and then with I_2. The Mn is precipitated as MnO_2 and the Fe remains in solution. Ferrocyanides precipitate white manganous ferrocyanide, $Mn_2Fe(CN)_6$, soluble in HCl. Precipitation may also be effected from a solution containing tartrate, to which NH_4OH has recently been added (distinction from Fe). Ferricyanides precipitate brown manganous ferricyanide, $Mn_3[Fe(CN)_6]_2$, insoluble in acids (separation from Co, Ni and Zn), but decomposed by hot, concentrated HCl. If an alkali or alkali carbonate be present, $K_3Fe(CN)_6$ oxidizes Mn^{++} to MnO_2, the $Fe(CN)_6^{-3}$ becoming $Fe(CN)_6^{-4}$. Ferrocyanides reduce MnO_4^{--} and MnO_4^- to Mn^{++}.

c. Nitric acid is of value in analysis of Mn compounds in that, as a non-reducing acid, it acts readily with oxidizing agents (PbO_2, ClO_3^-, etc.)

[1] Tartrates, etc., interfere.
[2] Cf. Friend, VIII, 313; Rüdisüle, V, 399.

to convert Mn to MnO_2 or MnO_4^-. Reducing agents (Cl^-, Br^-, etc.) should be absent. Sulfuric acid may be used in place of HNO_3.

$$(1)\ 2\,Mn(NO_3)_2 + 5\,PbO_2 + 6\,HNO_3 = 2\,HMnO_4 + 5\,Pb(NO_3)_2 + 2\,H_2O$$

$$(2)\ 5\,MnSO_4 + 2\,KClO_3 + H_2SO_4 + 4\,H_2O = 5\,MnO_2 + K_2SO_4 + Cl_2 + 5\,H_2SO_4$$

If an excess of alkali nitrite is added to a neutral solution of Mn^{++} at room temperature, a yellow liquid is obtained, that, on addition of oxalic acid, becomes deep cherry red, due to the formation of $Mn_2(C_2O_4)_3$. The color is quite permanent and the reaction has been suggested[1] for the detection of small amounts of Mn in the presence of much Fe.

d. Hypophosphorous acid reduces all higher forms of Mn to Mn^{++}. Alkali phosphates, Na_2HPO_4, precipitate, from neutral solutions of Mn^{++}, normal manganous phosphate, $Mn_3(PO_4)_2$, white, slightly soluble in H_2O; soluble in dilute acids. It turns brown on exposure to the air. From hot, acid solution containing Mn^{++}, NH_4^+ and PO_4^{-3}, slow addition of dilute NH_4OH will precipitate $MnNH_4PO_4$. The precipitation is quantitative in slightly alkaline solution (cf. 9).

e. Hydrosulfic acid precipitates manganous sulfide, MnS, pink, from an NH_4OH solution containing Mn^{++}, incompletely from a neutral acetate solution, and not in the presence of acetic acid, since MnS is soluble in solutions of low acidity (i.e., the $[S^{--}]$ from MnS is greater than the $[S^{--}]$ from H_2S, hence, the formation of H_2S takes place at the expense of the MnS). Acetic acid acting on the precipitated sulfides, MnS, CoS, NiS and ZnS, separates Mn from Co and Ni, and from the greater part of the Zn. All the higher oxidized forms of Mn (in solution or freshly precipitated), are reduced to Mn^{++} by S^{--}: $2\,KMnO_4 + 7\,(NH_4)_2S + 8\,H_2O = 2\,MnS + 2\,KOH + 14\,NH_4OH + 5\,S$. Green manganous sulfide is formed by the action of H_2S on a hot ammoniacal Mn^{++} solution,[2] also in the reduction of MnO_4^{--} and MnO_4^- in alkaline solution by S^{--}. MnS exposed to the air is oxidized: $MnS + air = Mn_2O_3 + MnSO_4 + S$. Soluble sulfites precipitate from solutions of Mn^{++}, manganous sulfite, $MnSO_3$, white, insoluble in H_2O, soluble in acids. Solutions of MnO_4^{--} or MnO_4^- are immediately reduced to MnO_2 by SO_3^{--} or $S_2O_3^{--}$; if an acid is present, the reduction is to Mn^{++}, in alkaline solution MnO_2 is formed: $8\,KMnO_4 + 3\,Na_2S_2O_3 + H_2O = 3\,Na_2SO_4 + 3\,K_2SO_4 + 8\,MnO_2 + 2\,KOH$.[3] If a manganous solution free from halides, be treated with a persulfate, the Mn^{++} is oxidized to MnO_2 (Eq. 1). If, however, a small amount of Ag^+ is

[1] Prandtl, *Ber.*, **49**, 1613–4 (1916).

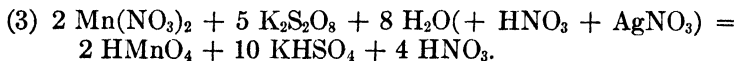
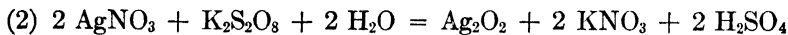
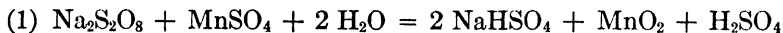
[2] Cf. Landesen, *Z. anorg. allgem. Ch.*, **193**, 277–96 (1930), *C.A.* **25**, 2656; Fischer, *J. Russ. Phys. Ch. Soc.*, **46**, 1481–1519 (1914), *C.A.* **9**, 2197.

[3] Kiliani, *Ch. Ztg.*, **32**, 1018 (1908).

present, the persulfate will oxidize this to silver peroxide[1] (Eq. 2), which in turn will change the Mn^{++} to MnO_4^- (Eq. 3). The test is very delicate but fails with moderate or large amounts of Mn due to precipitation of MnO_2.[2] An excess of Mn^{++} or Ag^+ will result in the precipitation of MnO_2 or Ag_2O_2, respectively.

(1) $Na_2S_2O_8 + MnSO_4 + 2\ H_2O = 2\ NaHSO_4 + MnO_2 + H_2SO_4$

(2) $2\ AgNO_3 + K_2S_2O_8 + 2\ H_2O = Ag_2O_2 + 2\ KNO_3 + 2\ H_2SO_4$

(3) $2\ Mn(NO_3)_2 + 5\ K_2S_2O_8 + 8\ H_2O(+\ HNO_3 + AgNO_3) =$
$2\ HMnO_4 + 10\ KHSO_4 + 4\ HNO_3$.

f. The halogen acids, HCl, HBr and HI readily reduce the higher valences of Mn to Mn^{++}, with evolution of the corresponding halogen. When MnO_2 is dissolved in cold, concentrated HCl, the dark, brownish-colored solution is said to contain manganese trichloride, $MnCl_3$[3] (cf. 4). It deposits MnO_2 on dilution with H_2O, and on warming, decomposes into $MnCl_2$ and Cl_2. When HCl reacts with MnO_4^-, the products depend upon the relative proportion of the interacting compounds. If MnO_4^- is in excess, MnO_2 is obtained: $2\ KMnO_4 + 8\ HCl = 2\ KCl + 2\ MnO_2 + 3\ Cl_2 + 4\ H_2O$. If HCl is in excess, the reaction becomes: $2\ KMnO_4 + 16\ HCl = 2\ KCl + 2\ MnCl_2 + 5\ Cl_2 + 8\ H_2O$.[4] Soluble iodides instantly reduce MnO_4^-, forming MnO_2 and IO_3^- (distinction from Cl^- and Br^-). Hypochlorites oxidize Mn^{++} to MnO_2 or, if Ag^+ is present, to MnO_4^-. If excess NaOH and Br_2 are added to a solution containing Mn^{++} and Cu^{++} the Mn is oxidized to MnO_4^-. A chlorate or bromate, when boiled with concentrated HNO_3 or H_2SO_4 and Mn^{++}, forms MnO_2. The precipitation is quantitative. In hot HNO_3 or H_2SO_4 solution, potassium periodate readily oxidizes Mn^{++} to purple MnO_4^-. This procedure is more dependable than the persulfate method.[5]

g. Soluble arsenites precipitate manganous arsenite, and arsenates precipitate manganous arsenate, insoluble in H_2O, soluble in acids. Solutions of AsO_3^{-3} reduce MnO_4^{--} and MnO_4^- to MnO_2, or Mn^{++}, depending upon conditions.

h. Solutions of CrO_4^{--} with Mn^{++}, shortly after mixing, form a dark brown precipitate, soluble in acids and NH_4OH. This product is not the normal manganous chromate.[6] No precipitate is obtained with dichromate ion.

[1] Showalter, *Z. Nahr.- und Genussm.*, **27**, 553–62 (1914), *C.A.* **8**, 3167; Applebaum, *Ch. Analyst*, **17**, 22 (1916).

[2] Bertiaux, *Bull. soc. ch.*, **35**, 1335 (1925), was able to oxidize 100 mg. of Mn in 200 cc. volume with H_3PO_4 present. Cf. Bright and Larrabee, *Bur. Standards J. Research*, **3**, 575 (1929).

[3] Cf. Friend, VIII, 272.

[4] Venable and Jackson, *J. Am. Ch. Soc.*, **42**, 237–9 (1920).

[5] Willard and Greathouse, *J. Am. Ch. Soc.*, **39**, 2366 (1917).

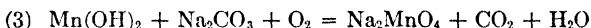
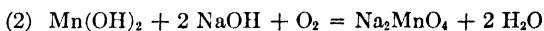
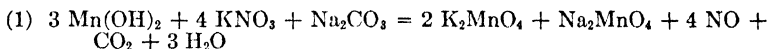
[6] Groger, *Z. anorg. allgem. Ch.*, **44**, 453 (1905).

i. Soluble manganates and permanganates precipitate Mn^{++} as MnO_2, being themselves reduced to the same form: $3\,MnSO_4 + 2\,KMnO_4 + 2\,H_2O = 5\,MnO_2 + 2\,KHSO_4 + H_2SO_4$.

7. Ignition. — Fusion with alkali and an oxidizing agent forms a bright green mass of alkali manganate. This constitutes a delicate and convenient test for Mn in any combination. If Mn forms but a small part of the material to be tested, it is better to apply the test to the MnO_2 separated in Group IV. A convenient form of test is by ignition on Pt° foil with an alkali nitrate and carbonate (Eq. 1). Ignition in the oxidizing flame with NaOH on platinum foil, effects the same result, less quickly and perfectly however (Eq. 2). Ignition in the oxidizing flame of a blowpipe, with a bead of Na_2CO_3, also gives the green color (Eq. 3).

(1) $3\,Mn(OH)_2 + 4\,KNO_3 + Na_2CO_3 = 2\,K_2MnO_4 + Na_2MnO_4 + 4\,NO + CO_2 + 3\,H_2O$

(2) $Mn(OH)_2 + 2\,NaOH + O_2 = Na_2MnO_4 + 2\,H_2O$

(3) $Mn(OH)_2 + Na_2CO_3 + O_2 = Na_2MnO_4 + CO_2 + H_2O$

With beads of borax or microcosmic salt before the outer blowpipe flame, Mn colors the bead violet while hot, amethyst red when cold.[1] The color is slowly destroyed by application of the inner reducing flame.

8. Detection. — *a.* After removal of the ions of Groups I–III metals, the Mn, with Co, Ni and Zn, is precipitated by H_2S from the ammoniacal Group III filtrate. Digestion in cold 1 *N* HCl dissolves MnS and ZnS. After removal of the H_2S by boiling, the solution is treated with an excess of NaOH and an oxidizing agent (Br_2, H_2O_2, ClO^-, etc.). The Mn is precipitated as MnO_2 while Zn remains in solution as ZnO_2^{--}. After filtration and washing, the MnO_2 is dissolved in HNO_3 and H_2O_2 and the solution tested for Mn by either the red lead,[2] persulfate,[3] or periodate test.[4] In the absence of reducing agents, or upon their removal, these tests may be applied to portions of the original solution.

b. If dilute NaOH in slight excess is added to a solution containing Mn^{++} and then boiled and filtered, the filter paper, upon moistening with benzidine acetate, will turn blue.[5, 6]

9. Determination. — *Gravimetrically*, Mn may be determined by conversion to Mn_3O_4, MnS, or $MnSO_4$ and weighing as such. Precipitation as $MnNH_4PO_4$ and ignition to $Mn_2P_2O_7$ is probably more satisfactory, however.[7] *Volumetric methods* are the most important for the determination of Mn. Almost all are based upon the fact that a very small amount of MnO_4^- imparts a deep purple color to a solution, and that Mn^{++} is

[1] Bancroft and Nugent, *J. Phys. Ch.*, **33**, 481–97 (1929); Curtman and St. John, *J. Am. Ch. Soc.*, **34**, 1675–9 (1912), state that the test will detect Mn, 1 part in 60,000.

[2] Curtman and St. John, *loc. cit.*, state that 1 part of Mn in 2.5 million can be detected, but that excess Fe seriously interferes.

[3] Dobbin, *Ch. News*, **113**, 133–4 (1916), gives the history of this test.

[4] The bismuthate test is not extensively used in qualitative analysis.

[5] Feigl, *Ch. Ztg.*, **44**, 689 (1920); cf. Ditz, *Ibid.*, **46**, 121–2 (1922).

[6] The "diamine" and tetralin tests for Mn have been summarized by Gutzeit, *Helv. Ch. Acta*, **12**, 713–40 (1929); cf. *C.A.* **23**, 4644.

[7] Hillebrand and Lundell, p. 349–50.

practically colorless. The bismuthate method involves oxidation of Mn^{++} to MnO_4^- by sodium bismuthate in HNO_3 solution, removal of the excess oxidizer by filtration, addition of an excess of standardized $FeSO_4$, and titration of the excess with standardized $KMnO_4$.[1] The persulfate method involves oxidization of Mn^{++} by $S_2O_8^{--}$ and Ag^+, and titration of the MnO_4^- with arsenite. *Colorimetrically*, small amounts of Mn may be readily determined by oxidation to MnO_4^- and comparison with a standard. Potassium periodate is one of the best reagents for the oxidation.[2]

10. Oxidation and Reduction. — (a) Mn^{++} is oxidized[3] to Mn^{+3} in alkaline solution on exposure to air;[4] to Mn^{+4} in neutral solution by MnO_4^{--} or MnO_4^-; in alkaline mixture by Cl, Br, I, $Fe(CN)_6^{-3}$, ClO^-,[5] BrO^-,[6] H_2O_2, etc.; in acid solution by boiling with concentrated HNO_3 or H_2SO_4 and ClO_3^- or BrO_3^-. Mn^{6-n} is oxidized to MnO_4^{--} by fusion with an alkali and an oxidizing agent, or by fusion with a chlorate alone. Mn^{7-n} is oxidized to MnO_4^- by warming with PbO_2 (or Pb_3O_4), a persulfate and Ag^+, or a periodate in either HNO_3 or H_2SO_4 solution. The oxidizing agent should be in excess, otherwise MnO_2 may be obtained. A solution of MnO_4^{--} decomposes into MnO_4^- and MnO_2 on standing, more rapidly on warming, dilution with H_2O or acidification. (b) All compounds of Mn having a higher state of oxidation than Mn^{++} are reduced to that form by $C_2O_4^{--}$, H_3PO_2, S^{--},[7] SO_3^{--}, H_2O_2 (in neutral or alkaline solutions to Mn^{+4}), Cl^-, Br^-, I^-, CNS^-, Hg_2^{++}, Sn^{++}, AsO_3^{-3},[8] Sb^{+3}, Cu_2^{++}, Fe^{++}, Cr^{++}, Cr^{+3},[9] Tl^+, etc.; the reducing agent becoming respectively, CO_2, PO_4^{-3}, S° to SO_4^{--} (depending upon temperature, concentration, etc.), Cl_2, Br_2, I_2, HCN and SO_4^{--}, Hg^{++}, Sn^{+4}, AsO_4^{-3}, Sb^{+5}, Cu^{++}, Fe^{+3}, $Cr_2O_7^{--}$. Mn with a valence greater than four is reduced to that state (or lower), by H_2, AsH_3, SbH_3, PH_3, SO_3^{--}, $S_2O_3^{--}$, NH_4OH,[10] Mn^{++},[11] etc. MnO_4^- is reduced to MnO_4^{--} on boiling with a fixed alkali: $4\ KMnO_4 + 4\ KOH = 4\ K_2MnO_4 + 2\ H_2O + O_2$; also by treating the alkaline solution with a few drops of I^- or dilute CH_2O. All of the common metals reduce MnO_4^- in acid solution; in dilute, neutral solution, even finely divided Pt and Au react.[12]

[1] *Ibid.*, p. 343–6.
[2] Willard and Greathouse, *J. Am. Ch. Soc.*, **39**, 2366 (1917).
[3] Cf. Orlovskii, *J. Russ. Phys. Ch. Soc.*, **61**, 1185–97 (1929), *C.A.* **24**, 542.
[4] Lenher, *J. Am. Ch. Soc.*, **38**, 638–40 (1916).
[5] To MnO_4^- if Ag^+ or Cu^{++} is present.
[6] To MnO_4^- if Cu^{++} is present.
[7] Dunnicliff and Nijhawan, *J. Ch. Soc.*, **1926**, 1–7.
[8] Reinitzer and Hoffmann, *Z. anal. Ch.*, **77**, 407–41 (1929).
[9] Fales and Roller, *J. Am. Ch. Soc.*, **51**, 345–59 (1929).
[10] Herschkowitsch, *Z. physik. Ch.*, **65**, 93–6 (1908), *C.A.* **3**, **606**.
[11] Fischer, *Ch. Ztg.*, **36**, 306 (1912), *C.A.* **7**, 1683–4.
[12] Foster, *Ch. News*, **115**, 73 (1917), *C.A.* **11**, **2074**.

§135. Zinc (Ger. *zink*). Zn = 65.38. Atomic No. 30. Valence 2. Identified by Homberg in 1695.[1]

1. Physical Properties. — Density, 7.1400 ± 0.0_36 at 16.3°;[2] melting point, 419.45°;[3] boiling point, 918°.[4] Zinc is a bluish-white metal, retaining its luster in dry air, but slightly tarnished in moist air or in H_2O. When heated to the boiling point with excess of air, it burns with a bluish flame to ZnO. Zinc dust, mixed with sulfur, is ignited by percussion; if finely divided, the dust forms an explosive mixture with moist air. At room temperature, zinc breaks with a coarse crystalline fracture. It is malleable at 150° and may be rolled into sheets or drawn into wire. Above 180° it changes, and at 205° is so brittle that it may be powdered easily.

Zinc is used extensively in laboratories for the generation of hydrogen. The pure metal is not suitable for this purpose because the reaction proceeds too slowly.[5] Impurities render the metal readily soluble in acids. Traces of Pt or Au have a pronounced accelerating effect; also, a few drops of dilute $CuSO_4$ will insure a smooth, rapid evolution of hydrogen. Commercially, the chief uses for zinc are as a protective coating for iron ("galvanized iron"); a constituent of various alloys, the chief one being brass; for the precipitation of more noble metals by displacement; as a component of paint (ZnO pigment and lithopone); as the negative element in dry cells.

2. Occurrence. — The more important zinc ores are sphalerite or zinc blende, ZnS; and smithsonite, $ZnCO_3$; of less importance are franklinite, $(FeMnZn)(FeO_2)_2$; zincite, ZnO; hemimorphite or calamine,[6] $H_2Zn_2SiO_5$. In 1929 the world's supply of zinc came chiefly from the United States, Belgium, Poland and Germany. The total production was about 1.5 million metric tons, of which the countries mentioned furnished over two-thirds. The price normally is 5¢–8¢ per pound.

3. Preparation. — Subject to modification, dependent on the nature of the material to be treated, zinc ores are handled in two ways: (1) After concentration, the ore is roasted to ZnO, which is mixed with coal, and heated to about 1200°: $ZnO + C = Zn + CO$. The vaporized Zn is condensed and cast into blocks called "spelter." (2) The zinc ore is converted to $ZnSO_4$ (by low temperature roasting), which is leached out and electrolyzed. The metal is deposited from acid solution at high current density; it may have a purity of over 99.9%.[7, 8]

4. Oxides and Hydroxides. — Zinc oxide, ZnO, white, is obtained by igniting, in the air, either Zn°, the hydroxide, carbonate, nitrate, oxalate, sulfide, or any of its organic oxysalts, etc. Zinc hydroxide,[9] $Zn(OH)_2$, is made from solutions of Zn^{++} by precipitation with fixed alkalis (cf. 6, *a*). The hydroxide is amphoteric.

5. Solubilities. — *a. Metal.* — Pure Zn dissolves very slowly in acids or alkalis. Impurities, or contact with Cu, Pt, etc., accelerate the reaction, hence the ready solution of commercial Zn. In contact with Fe it is quite rapidly oxidized in water containing air, but is not dissolved by pure water. It dissolves in dilute HCl (see above), H_2SO_4 and acetic acid (Eq. 1), and in alkaline solutions, with evolution of H_2 (Eq. 2); in very dilute HNO_3 without evolution of gas (Eq. 3); in moderately dilute, cold HNO_3 with evolution, chiefly, of N_2O (Eq. 4); and in more concentrated HNO_3 with evolution of NO (Eq. 5). Concentrated HNO_3 dissolves but little Zn, the nitrate being very sparingly soluble in that medium. Hot, concentrated H_2SO_4 dissolves Zn with evolution of SO_2 (Eq. 6).

[1] Hommel, *Ch. Ztg.*, **36**, 905–6, 918–20 (1912), *C.A.* **6**, 3039.

[2] Egerton and Lee, *Proc. Roy. Soc. (London)*, **A103**, 499 (1923).

[3] Cyr, *Trans. Am. Electroch. Soc.*, **52**, 349 (1927).

[4] Egerton, *Phil. Mag.*, [6] **33**, 471 (1917); cf. Gmelin, 8th ed., No. 32, p. 35; Friend, III, 2, p. 97.

[5] Evans, IV, 128–9.

[6] English mineralogists apply this name to the natural carbonate.

[7] Friend, III, 2, p. 94–5.

[8] Doerner, Bur. Mines, *Rept. of Investigations* 3091 (1931), has studied the reduction of ZnO to Zn° by means of CH_4 and natural gas.

[9] Dietrich and Johnston, *J. Am. Ch. Soc.*, **49**, 1419–31 (1927).

(1) $Zn + H_2SO_4 = ZnSO_4 + H_2$

(2) $Zn + 2\ NaOH = Na_2ZnO_2 + H_2$

(3) $4\ Zn + 10\ HNO_3 = 4\ Zn(NO_3)_2 + NH_4NO_3 + 3\ H_2O$

(4) $4\ Zn + 10\ HNO_3 = 4\ Zn(NO_3)_2 + N_2O + 5\ H_2O$

(5) $3\ Zn + 8\ HNO_3 = 3\ Zn(NO_3)_2 + 2\ NO + 4\ H_2O$

(6) $Zn + 2\ H_2SO_4 = ZnSO_4 + SO_2 + 2\ H_2O$

b. Oxide and Hydroxide. All reagents that dissolve the metal also dissolve its oxide and hydroxide. They are also soluble in solutions of ammonium salts.

c. Salts. — The halides (fluoride excepted), chlorate, nitrate (6 H_2O), and acetate (7 H_2O) are deliquescent; the sulfate (7 H_2O) is efflorescent. The chloride is readily soluble in alcohol in all proportions. The sulfide, basic carbonate, phosphate, arsenate, oxalate, periodate, cyanide, and ferrocyanide are insoluble in H_2O; the sulfite is sparingly soluble. The ferrocyanide is insoluble in HCl. The sulfide is almost insoluble in dilute acetic acid (separation from MnS). All Zn salts are soluble in the fixed alkalis except ZnS; and all in NH_4OH except ZnS and $Zn_2Fe(CN)_6$. The most stable complex ions of Zn are $Zn(NH_3)_4^{++}$, $Zn(CN)_4^{--}$, and $HZnO_2^-$.

6. Reactions. — *a.* The alkali hydroxides precipitate zinc hydroxide, $Zn(OH)_2$, white, soluble in excess of the reagent, forming a zincate:[1] $ZnCl_2 + 2\ NaOH = Zn(OH)_2 + 2\ NaCl$; $Zn(OH)_2 + NaOH = NaHZnO_2 + H_2O$. The precipitate of $Zn(OH)_2$ dissolves more readily in excess of the alkalis at room temperature than when heated. An alkali solution as dilute as 0.1 *N* does not dissolve $Zn(OH)_2$, no matter how great an excess is added. Ammonium hydroxide precipitates, from solutions containing no NH_4^+, part of the Zn^{++} as $Zn(OH)_2$. If excess of the reagent is added, the $Zn(OH)_2$ dissolves, due to the formation of the complex ion, $Zn(NH_3)_4^{++}$. Should sufficient NH_4^+ be present in the original solution before the addition of NH_4OH, no precipitation will take place.[2]

Alkali carbonates precipitate, from solutions of Zn^{++}, a basic carbonate, $5ZnO{\cdot}2CO_2{\cdot}4H_2O$,[3] white, soluble in $(NH_4)_2CO_3$, readily in alkali hydroxides. Carbonates of the alkaline earth metals have no action at room temperature, but upon boiling, precipitate all of the Zn^{++}.

b. Solutions of oxalate ion precipitate Zn^{++} as white zinc oxalate, $ZnC_2O_4{\cdot}2H_2O$, soluble in acids and alkalis. Alkali cyanides precipitate zinc cyanide, $Zn(CN)_2$, white, soluble in excess of the reagent, forming $Zn(CN)_4^{--}$. Alkali ferrocyanides precipitate zinc ferrocyanide,

[1] Cf. Hildebrand and Bowers, *J. Am. Ch. Soc.*, **38**, 785–8 (1916); Goudriaan, *Rec. trav. ch.*, **39**, 505–14 (1920), *C.A.* **15**, 479.

[2] Stasevich, *J. Russ. Phys. Ch. Soc.*, **43**, 354–62 (1911), *C.A.* **6**, 13.

[3] Kraut, *Z. anorg. allgem. Ch.*, **13**, 1 (1896); Mikusch, *Ibid.*, **56**, 365 (1907).

$Zn_2Fe(CN)_6$, white.[1] Alkali ferricyanides precipitate zinc ferricyanide, $Zn_3[Fe(CN)_6]_2$, yellowish.

d. Slow addition of NH_4OH to neutralize an acid solution containing Zn^{++} and PO_4^{-3}, results in the precipitation of $ZnNH_4PO_4$, white. The precipitation is quantitative. Under other conditions $Zn_3(PO_4)_2$ may be precipitated.[2] It is soluble in alkali hydroxides and nearly all acids.

e. Hydrosulfic acid precipitates some of the Zn^{++} as ZnS, white, from solutions, not too acid; in the presence of sufficient alkali acetate to take care of the H^+, precipitation will be complete. In alkaline solution, the precipitation of Zn^{++} by S^{--} is complete,[3] although a large excess of either NH_4OH or NaOH tends to inhibit the reaction. The same is true of certain salts, e.g., NaCl.[4] Concentrated solutions of Na_2SO_3 precipitate Zn^{++} as a basic zinc sulfite; if the solution is too dilute for immediate precipitation, boiling will cause the formation of a bulky white precipitate of the basic sulfite.

f. Potassium periodate gives a white precipitate with Zn^{++}. In the cold, NH_4^+ and NH_4OH prevent precipitation, but boiling overcomes their interference.

g. Zn^{++} is precipitated by arsenite or arsenate ion, forming the corresponding salt, white, gelatinous, readily soluble in alkalis and acids, including arsenic acids.

h. Normal chromates form, with Zn^{++}, a yellow precipitate of zinc chromate, readily soluble in acids and alkalis. No precipitate is obtained with $Cr_2O_7^{-}$

7. Ignition. — With Na_2CO_3, on charcoal, before the blowpipe, compounds of Zn are reduced to the metallic state. The metal is vaporized and then oxidized in the air, and deposited as ZnO, yellow when hot, white when cold. If this coating, or ZnO otherwise prepared, is moistened with $Co(NO_3)_2$ and again ignited, it assumes a green color. With borax or microcosmic salt, Zn compounds give a bead that, if strongly saturated, is yellowish when hot and opaque white when cold.

8. Detection. — After the removal of Groups I–III, Zn is precipitated with Co, Ni and Mn from the ammoniacal Group III filtrate by H_2S. Digestion of the precipitate with cold, dilute HCl dissolves the MnS and ZnS. Then the solution is boiled to eliminate H_2S, and the Zn changed to $NaHZnO_2$ by an excess of NaOH (plus some Br_2, H_2O_2, or ClO^-), which precipitates the Mn^{++} as MnO_2. The excess oxidizing agent is removed and the resulting solution tested for Zn^{++}, generally by addition of H_2S to give ZnS.

[1] Mehlig, *J. Ch. Ed.*, **4**, 722 (1927), discusses the use of ferrocyanide as a confirmatory test for Zn.

[2] Eberly, *et al.*, *J. Am. Ch. Soc.*, **42**, 1433 (1920).

[3] Cf. McCay, *J. Am. Ch. Soc.*, **30**, 376–8 (1908), in discussing the action of H_2S on alkaline solutions of Zn salts, calls attention to the solubility of ZnS in excess sulfide.

[4] Dede, *Ber.*, **61B**, 2248–51 (1928).

b. Organic reagents suggested for the detection of Zn^{++} include diphenylamine,[1] diphenylthiocarbazone,[2] resorcinol,[3] 8-hydroxyquinoline,[4] etc.

9. Determination. — *Gravimetrically*, zinc may be (1) precipitated in neutral solution as $ZnNH_4PO_4$, ignited to $Zn_2P_2O_7$, and weighed as such; (2) precipitated as the sulfide[5] from dilute H_2SO_4 or formic acid solution, converted to the oxide or sulfate,[6] and weighed as such. *Volumetric methods* are (1) titration with $K_4Fe(CN)_6$,[7] the endpoint being determined potentiometrically or by use of uranyl acetate as an external indicator; (2) titration with Na_2S.[8] The electrolytic deposition of Zn is unsatisfactory because complete precipitation is difficult to attain.

10. Oxidation and Reduction. — Metallic Zn precipitates the free metal from solutions of Cd, Sn, Pb, Cu, Bi, Hg, Ag, Pt, Au, Sb, Te, In, Fe, Co, Ni, Pd, Rh, Ir and Os.[9] Zinc with Cu (Zn-Cu couple), reduces NO_3^- and NO_2^- to NH_3, ClO_3^- to Cl^-, IO_3^- to I^-, $Fe(CN)_6^{-3}$ to $Fe(CN)_6^{-4}$, etc. In the presence of a non-reducing acid, CrO_4^{--} is reduced to Cr^{+3}, Fe^{+3} to Fe^{++}, and compounds of Mn higher than bivalent, to Mn^{++}. Zinc is precipitated as the metal from an acetic acid solution by Mg. The oxide is reduced to Zn° by heating in a stream of hydrogen.

[1] Cone and Cady, *J. Am. Ch. Soc.*, **49**, 2214–5 (1927).
[2] Fischer, see: *C.A.* **20**, 3660.
[3] Cerdan, *Répert. pharm.*, [3] **22**, 4–5 (1910), *C.A.* **4**, 2079 (1910).
[4] *Berg, J. prakt. Ch.*, **115**, 178 (1927); *Z. anal. Ch.*, **71**, 171 (1927).
[5] Fales and Ware, *J. Am. Ch. Soc.*, **41**, 487–99 (1919); Urbasch, *Ch. Ztg.*, **46**, 6, 29, 53, 97, 101, 125, 133, 138 (1922).
[6] Gutbier and Staib, *Z. anal. Ch.*, **61**, 97–103 (1922).
[7] Kolthoff and Verzijl, *Rec. trav. ch.*, **43**, 389–93 (1924), *C.A.* **18**, 2482; Springer, *Z. angew. Ch.*, **30**, i, 173 (1917).
[8] Beckurts, 2nd ed. (1931), p. 411.
[9] Gmelin, 8th ed., No. 32, p. 66, *et seq.*

§136. Comparison of Certain Reactions of the Metals of Groups III-IV.*

	Al^{+3}	Cr^{+3}	$Cr_2O_7^{--}$	Fe^{+3}	Fe^{++}	Mn^{++}	Co^{++}	Ni^{++}	Zn^{++}
NaOH	$Al(OH)_3$ white $NaAlO_2$ colorless	$Cr(OH)_3$ green $NaCrO_2$ green	CrO_4^{--} yellow	$Fe(OH)_3$ red brown	$Fe(OH)_2$ white	$Mn(OH)_2$ white	$Co(OH)_2$ pink	$Ni(OH)_2$ green	$Zn(OH)_2$ white $NaHZnO_2$ colorless
NH_4OH	$Al(OH)_3$ white	$Cr(OH)_3$ green	CrO_4^{--} yellow	$Fe(OH)_3$ red brown	$Fe(OH)_2$ white	$Mn(OH)_2$ white	$CoOHCl$ blue green $Co(NH_3)_4^{++}$ pink	$Ni(OH)_2$ green $Ni(NH_3)_6^{++}$ blue	$Zn(OH)_2$ white $Zn(NH_3)_4^{++}$ colorless
NH_4Cl + NH_4OH	$Al(OH)_3$ white	$Cr(OH)_3$ green	CrO_4^{--} yellow	$Fe(OH)_3$ red brown	$Fe(OH)_2$ white	n.v.a.	$Co(NH_3)_4^{++}$ pink	$Ni(NH_3)_6^{++}$ blue	$Zn(NH_3)_4^{++}$ colorless
Na_2CO_3 (or $(NH_4)_2CO_3$)	$Al(OH)_3$ white	$Cr(OH)_3$ green	CrO_4^{--} yellow	$Fe(OH)_3$ red brown	$FeCO_3$ white	$MnCO_3$ white	$CoCO_3$ pink	$NiCO_3$ green	$ZnCO_3$ white
H_2S (in *acid* soln.)	n.v.a.	n.v.a.	Cr^{+3} + S green white	Fe^{++} + S colorless white	n.v.a.	n.v.a.	n.v.a.	n.v.a.	n.v.a.
H_2S (in *alk.* soln., or $(NH_4)_2S$)	$Al(OH)_3$ white	$Cr(OH)_3$ green	$Cr(OH)_3$ + S green	Fe_2S_3 black	FeS black	MnS pink	CoS black	NiS black	ZnS white
Mild oxidizing agents	n.v.a.	n.v.a. (acid soln.) CrO_4^{--} yellow (alk. soln.)	n.v.a.	n.v.a.	Fe^{+3} yellow	n.v.a. (acid soln.) MnO_2 brown (alk. soln.)	n.v.a. (acid soln.) $Co(OH)_3$ black (alk. soln.)	n.v.a.	n.v.a.
Strong oxidizing agents	n.v.a.	$Cr_2O_7^{--}$ orange	n.v.a.	n.v.a. (FeO_4^{--}?) (alk. soln.)	Fe^{+3} yellow	MnO_4^- purple	n.v.a. (acid soln.) $Co(OH)_3$ black (alk. soln.)	n.v.a. (acid soln.) NiO_2 black (alk. soln.)	n.v.a.
Reducing agents	n.v.a.	n.v.a.	Cr^{+3} green	Fe^{++} colorless	n.v.a.	n.v.a.	n.v.a.	n.v.a.	n.v.a.

* Solutions of the chlorides, nitrates, or sulfates of the cations, and $K_2Cr_2O_7$, may be used.

Notes. — 1. In this table the letters *n.v.a.* mean no visible action; a straight line under a formula indicates that the substance precipitates; a line with upturned ends, that the substance is in solution; if both are used, the substance will not precipitate from dilute solutions.

2. When two formulas appear in a single square, the upper one indicates the first reaction that occurs; the lower one shows the further reaction that occurs with excess of reagent.

3. The text should be consulted for the further chemical and physical properties of these substances.

§137. Outline of the Analysis of Group IV
(Starting with the filtrate from Group III)

Metals, after removal of Groups I–III, whose sulfides precipitate with H_2S in ammonical solution in the presence of high concentration of NH_4Cl.

Metals	Zn	Mn	Co	Ni
Ions in acid solution	Zn^{++}	Mn^{++} MnO_4^-	Co^{++}	Ni^{++}
Ions in NaOH solution	ZnO_2^{--}	MnO_4^{--} MnO_4^-	——	——
Ions in NH_4OH solution	$Zn(NH_3)_4^{++}$.	——	$Co(NH_3)_4^{++}$	$Ni(NH_3)_6^{++}$

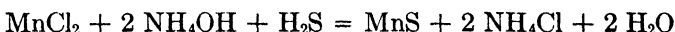
<table>
<tr><td colspan="4">Make solution about N with NH_4OH</td></tr>
<tr><td>Mn^{++}</td><td>$Zn(NH_3)_4^{++}$</td><td>$Co(NH_3)_4^{++}$</td><td>$Ni(NH_3)_6^{++}$</td></tr>
<tr><td colspan="4">H_2S</td></tr>
<tr><td>$\underline{MnS}$</td><td>$\underline{ZnS}$</td><td>$\underline{CoS}$</td><td>$\underline{NiS}$</td></tr>
<tr><td colspan="4">HCl</td></tr>
<tr><td>$MnCl_2$</td><td>$ZnCl_2$</td><td>$\underline{CoS}$</td><td>$\underline{NiS}$</td></tr>
<tr><td colspan="2">$NaOH + Br_2$</td><td colspan="2">$HCl + HNO_3$</td></tr>
<tr><td>$\underline{MnO_2}$</td><td>Na_2ZnO_2</td><td>$CoCl_2$</td><td>$NiCl_2$</td></tr>
<tr><td>$HNO_3 + H_2O_2$</td><td>$NH_4OH + H_2S$</td><td colspan="2">Divide into 2 parts</td></tr>
<tr><td>$Mn(NO_3)_2$</td><td>$\underline{ZnS}$</td><td>NH_4CNS</td><td>$NH_4OH+C_4H_8N_2O_2$</td></tr>
<tr><td>$HNO_3 + Pb_3O_4$</td><td></td><td>$(NH_4)_2Co(CNS)_4$</td><td>$\underline{Ni(C_4H_7N_2O_2)_2}$</td></tr>
<tr><td>$HMnO_4$</td><td></td><td></td><td></td></tr>
</table>

DIRECTIONS FOR THE PRECIPITATION AND ANALYSIS OF THE FOURTH GROUP

§138. In the directions given below it is assumed that Groups I–III have been present and removed in the usual manner, the final filtrate being used for the precipitation of Group IV. If one wishes to examine a solution directly for Group IV, with Groups I–III known to be absent, account must be taken of the forms in which Group IV metals may be present. Thus, MnO_4^- and MnO_4^{--}, identified by color, should be reduced to Mn^{++} by $CH_2O + HCl$. Any strongly ammoniacal solution may well be neutralized with HCl, then made *N* with respect to NH_4OH. If the original solution is strongly alkaline, but not ammoniacal, it should be neutralized with HCl, and made *N* with respect to both NH_4Cl and NH_4OH. This avoids the possibility of precipitating Group V as sulfides in Group IV.

Manipulation. — To the filtrate from Group III (§128) add 5 cc. of 5 *N* NH_4OH, pass in H_2S for 0.5–1 minute, filter, and test the filtrate with H_2S for completeness of precipitation. If further precipitate forms pass in H_2S for 0.5–1 minute, filter and test again with H_2S. CoS and NiS are black, MnS is light pink, and ZnS is white.

$$Co(NH_3)_4Cl_2 + H_2S = CoS + 2\ NH_4Cl + 2\ NH_3$$

$$MnCl_2 + 2\ NH_4OH + H_2S = MnS + 2\ NH_4Cl + 2\ H_2O$$

The filtrate is marked and set aside to be tested for Group V (§191).

Wash the precipitate with 1% NH_4Cl solution containing a little $NH_4OH + H_2S$. Transfer to a small beaker, cover with 20 cc. of water, and let stand several minutes. Then add 5 cc. of 5 *N* HCl with stirring, let stand 1–2 minutes, filter and wash. Manganese sulfide and ZnS dissolve readily, CoS and NiS only slowly. The filtrate is set aside to test for Zn and Mn (§142); the black precipitate is examined for Co and Ni (§140).

§139. Notes. — 1. Conditions for precipitation of Group IV differ from those in Group II. In Group II H_2S is passed into an acid solution in which the gas is only slightly soluble, so much of it escapes from the solution. In Group IV the solution is alkaline, therefore the H_2S is readily absorbed. Further, in Group IV, if too much H_2S is passed in, NiS forms a colloidal solution in part and runs through the filter. This may be avoided by passing in H_2S for only a short time before filtering and testing for completeness of precipitation.

2. If the filtrate is dark in color, Ni may be suspected immediately. In such a case the NiS may be coagulated by neutralizing with $HC_2H_3O_2$ and boiling. The resulting precipitate may be filtered out, washed, and tested directly for Ni or combined with the main precipitate for systematic analysis of Group IV.

3. Zinc and Mn sulfides usually form a fine suspension that runs through the ordinary filter paper with surprising readiness. On the other hand, CoS and NiS are usually flocculent and easy to filter. If the latter are present in appreciable quantity they help

retain ZnS and MnS on the filter, so refiltering once or twice is sufficient to give a perfectly clear filtrate. In their absence, however (which may be recognized by the fact that the Group IV precipitate is light colored), refiltering, or the use of double filters, is largely a waste of time. In such a case the solution should be treated in one of the two following ways before filtering is attempted: (1) Add to the solution 2–3 cc. of $BiCl_3$ solution, pass in H_2S again for 0.5–1 minute, then filter, refiltering if necessary until the filtrate is clear. (The Bi_2S_3 is flocculent and readily filtered, serving the same purpose as the CoS or NiS in retaining any ZnS or MnS.) (2) Prepare a suspension of paper pulp from part of a tablet of ashless filter paper (or by tearing a filter paper into small bits and boiling a short time with HCl, then diluting, filtering, washing and shaking the pulp with a little water). Add the paper pulp to the solution, stir and filter.

4. Freshly precipitated CoS and NiS dissolve fairly readily even in cold, normal HCl, but on standing they become more inert. The separation of Zn and Mn from Co and Ni is improved, therefore, by letting the Group IV precipitate stand a little while (5–10 minutes) before treating with HCl. If much Co or Ni is present some will always be found with the Mn and Zn, but there will be enough left as a precipitate to be readily identified (except that as much as 1–2 mg. of CoS, in the absence of MnS, may dissolve completely).

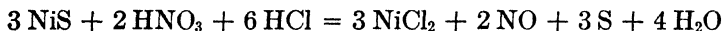
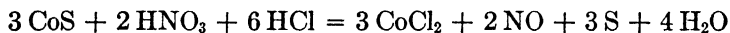
5. Lead, incompletely precipitated in Groups II and III, and any Fe not removed in Group III will precipitate in Group IV as black PbS and FeS. These do not interfere with the confirmatory tests for any of the Group IV metals, but sometimes cause the tests for Co and Ni to be repeated when these metals are absent.

6. If Cd is not completely precipitated in Group II it will appear in Group IV as a yellow or greenish-yellow precipitate. Part of it dissolves in the HCl and may appear as a white precipitate of $Cd(OH)_2$ when separating Zn from Mn.

7. Small amounts of Group V metals (Ba, Sr and Ca) may be lost by precipitation in Group IV as carbonates, due to $(NH_4)_2CO_3$ in the NH_4OH or formed by absorption of CO_2 by the alkaline solution, or as sulfates due to oxidation of the moist sulfides by oxygen of the air.

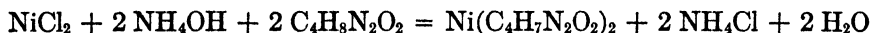
§140. Manipulation. — Transfer the precipitate of CoS and NiS (§138) to a casserole, add 5–10 cc. of 5 *N* HCl and 2–3 cc. 5 *N* HNO_3, heat to boiling, let boil gently until the reaction seems complete, filter and wash.

$$3\,CoS + 2\,HNO_3 + 6\,HCl = 3\,CoCl_2 + 2\,NO + 3\,S + 4\,H_2O$$

$$3\,NiS + 2\,HNO_3 + 6\,HCl = 3\,NiCl_2 + 2\,NO + 3\,S + 4\,H_2O$$

Return the solution to the casserole, evaporate barely to dryness, and dissolve the residue in 10 cc. of H_2O, adding 1–2 drops of HCl if necessary. Divide the solution into two parts testing one for Co and the other for Ni. To the first portion add 2 g. of solid NH_4CNS and 2 cc. of amyl alcohol, shake thoroughly and then let stand until the alcohol layer forms again. A sky blue color indicates Co.

$$CoCl_2 + 4\,NH_4CNS = (NH_4)_2Co(CNS)_4 + 2\,NH_4Cl$$

To the second portion add 5 cc. of NH_4Cl, plus NH_4OH till slightly alkaline, then 2 cc. of a 1% solution of dimethylglyoxime in alcohol. If Ni is present a scarlet precipitate will form.

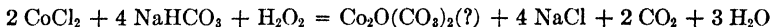
$$NiCl_2 + 2\,NH_4OH + 2\,C_4H_8N_2O_2 = Ni(C_4H_7N_2O_2)_2 + 2\,NH_4Cl + 2\,H_2O$$

§141. Notes. — 1. A large number of schemes have been worked out for the separation of Co and Ni from each other, but slow formation of precipitates or other objectionable features make them rather unsatisfactory. One of the best of these procedures uses

KNO_2 in acetic acid solution to precipitate Co as $K_3Co(NO_2)_6$ (yellow), leaving Ni in solution to be identified in the usual way. The tests for Co and Ni are delicate enough so that for qualitative analysis it is sufficient to test portions of the solution for the two metals, individually, without attempting preliminary separations.

2. Cobalt may be identified when the solution has been evaporated almost to dryness, by tilting the casserole and heating the bottom gently. As the film dries Co first forms pink crystals of $CoCl_2 \cdot 6H_2O$, but as these are heated gently they lose water and form a dark blue residue. Let cool, add a few drops of water and the blue color disappears.

3. Another test for Co consists in adding to a portion of the solution 2–3 times its volume of concentrated HCl (or saturating the solution with NH_4Cl and warming). A blue color forms, due to $CoCl_4^{--}$.

4. Another test for Co is carried out as follows: Add to a portion of the solution 1–2 g. of $NaHCO_3$ (more than enough to saturate the solution), shake, and then add 1–2 cc. of H_2O_2. A green solution indicates Co.

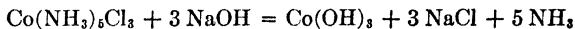
$$2\,CoCl_2 + 4\,NaHCO_3 + H_2O_2 = Co_2O(CO_3)_2(?) + 4\,NaCl + 2\,CO_2 + 3\,H_2O$$

If the green precipitate of $NiCO_3$ makes it difficult to judge the color of the solution, filter and note the color of the filtrate.

5. The test for Co described in the manipulation requires high concentration of NH_4CNS to be effective. For that reason the solid salt is added rather than a solution of the reagent, and the volume of solution being treated is kept small.

6. Sometimes the amyl alcohol layer is colored green or red instead of blue. This is due to Fe as a slight impurity in the reagents or in the solution. It can be removed fairly effectively by adding 0.5 cc. of $SnCl_2$ and shaking. This reduces the $Fe(CNS)_3$ to the colorless ferrous salt.

7. The two common ions of Co are Co^{++} and $Co(NH_3)_4^{++}$. They are distinguished from each other by the fact that the former is found only in neutral or acid solution, while the latter exists only in an ammoniacal solution. Both are pink or light red in color, but $Co(NH_3)_4^{++}$ is readily oxidized, even by O_2 of the air, turning brownish red and then deep red as the oxidation proceeds. Some of the NH_3 complexes of trivalent Co are surprisingly stable, not being decomposed by acidifying. Thus, $Co(NH_3)_5^{+3}$ may be in solution in the filtrate from Group 1, and on adding HCl and CH_2O and boiling to reduce $Cr_2O_7^{--}$ may form a dark red, crystalline precipitate of $Co(NH_3)_5Cl_3$. If this is encountered, the simplest way to handle it is to filter, transfer the precipitate to a casserole, add several cubic centimeters of NaOH and boil until the odor of NH_3 is gone. This converts the Co to $Co(OH)_3$ (black) which may be dissolved in acid with a few drops of H_2O_2 as reducing agent, and the usual tests for Co applied.

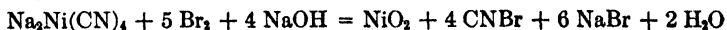
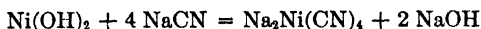
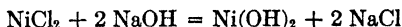
$$Co(NH_3)_5Cl_3 + 3\,NaOH = Co(OH)_3 + 3\,NaCl + 5\,NH_3$$

$$2\,Co(OH)_3 + 4\,HCl + H_2O_2 = 2\,CoCl_2 + 6\,H_2O + O_2$$

8. The test for Ni is interfered with seriously by Co, the latter metal combining with the dimethylglyoxime to form a soluble compound that does not yield a precipitate with Ni. Excess of the reagent is sometimes recommended to overcome the difficulty, but this is objectionable because the solution of the reagent is rather dilute and the reagent itself is quite expensive. Oxidation of the Co in ammoniacal solution by H_2O_2 to $Co(NH_3)_6^{+3}$ before trying the test for Ni helps slightly. A more effective and simpler procedure to test for small amounts of Ni in the presence of large amounts of Co consists in adding to 5–10 cc. of the neutral solution (free from NH_4^+, and containing 50–100 mg. of Co) 1–2 cc. of 5 *N* NH_4OH, filtering out the green basic salt of Co (CoOHCl), and testing the filtrate in the ordinary way for Ni. Most of the Co precipitates and most of the Ni stays in solution, so a definite test for Ni may be obtained with as little as 0.1–0.2 mg. of Ni present.

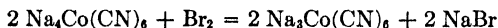
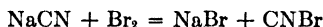
9. Another method of testing for Ni when Co is present: Add excess NaOH, then just sufficient NaCN to dissolve the precipitates of $Ni(OH)_2$ and $Co(OH)_2$, then add 5–10 cc. of bromine water, shake, and look for the formation of a black precipitate of NiO_2.

$$NiCl_2 + 2\,NaOH = Ni(OH)_2 + 2\,NaCl$$

$$Ni(OH)_2 + 4\,NaCN = Na_2Ni(CN)_4 + 2\,NaOH$$

$$Na_2Ni(CN)_4 + 5\,Br_2 + 4\,NaOH = NiO_2 + 4\,CNBr + 6\,NaBr + 2\,H_2O$$

The last reaction does not take place until the excess NaCN and the $Na_4Co(CN)_6$ have been oxidized, so the chief source of trouble is failure to add sufficient Br_2.

$$NaCN + Br_2 = NaBr + CNBr$$

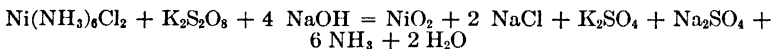
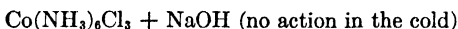
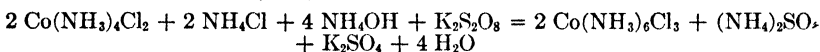
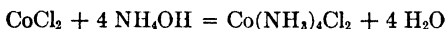
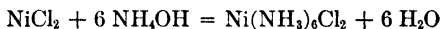
$$2\ Na_4Co(CN)_6 + Br_2 = 2\ Na_3Co(CN)_6 + 2\ NaBr$$

10. Another method of separating Ni from Co in which Co may be identified at the same time is the persulfate separation: Add 5 cc. of 5 *N* NH_4Cl + 10 cc. of NH_4OH + 0.5–1 g. of $K_2S_2O_8$ (or $(NH_4)_2S_2O_8$). Heat to boiling and keep hot until any color change is complete. Cool, add 10 cc. of 5 *N* NaOH, stir and let stand a few minutes. A black precipitate of NiO_2 will form. This may be filtered out, dissolved in HCl with the aid of a little H_2O_2, and the dimethylglyoxime test applied. Cobalt may precipitate slightly if present in large amounts, but will be largely or entirely present in the filtrate to which it imparts a characteristic red color.

$$NiCl_2 + 6\ NH_4OH = Ni(NH_3)_6Cl_2 + 6\ H_2O$$

$$CoCl_2 + 4\ NH_4OH = Co(NH_3)_4Cl_2 + 4\ H_2O$$

$$2\ Co(NH_3)_4Cl_2 + 2\ NH_4Cl + 4\ NH_4OH + K_2S_2O_8 = 2\ Co(NH_3)_6Cl_3 + (NH_4)_2SO_4 + K_2SO_4 + 4\ H_2O$$

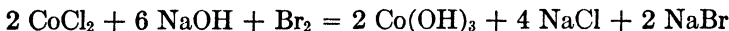
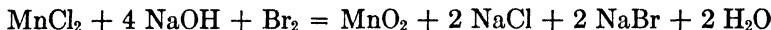
$Co(NH_3)_6Cl_3$ + NaOH (no action in the cold)

$$Ni(NH_3)_6Cl_2 + K_2S_2O_8 + 4\ NaOH = NiO_2 + 2\ NaCl + K_2SO_4 + Na_2SO_4 + 6\ NH_3 + 2\ H_2O$$

11. The common ions of Ni are Ni^{++} and $Ni(NH_3)_6^{++}$. The former is found in neutral or acid solution, the latter in ammoniacal solution.

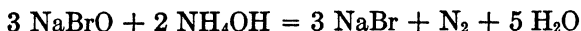
§142. **Manipulation.** — Boil the filtrate (§138) containing $MnCl_2$ and $ZnCl_2$ (and small amounts of $CoCl_2$ and $NiCl_2$) until the H_2S is completely removed (test with $Pb(C_2H_3O_2)_2$ paper), neutralize with NaOH, add 5–10 cc. excess NaOH, then add 5–10 cc. of Br_2-water and boil 1–2 minutes. Manganese precipitates as MnO_2 (chocolate color), Co and Ni as black $Co(OH)_3$ and NiO_2, Zn stays in solution as Na_2ZnO_2.

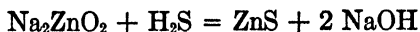
$$MnCl_2 + 4\ NaOH + Br_2 = MnO_2 + 2\ NaCl + 2\ NaBr + 2\ H_2O$$

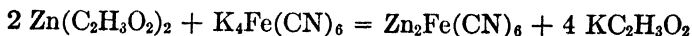
$$2\ CoCl_2 + 6\ NaOH + Br_2 = 2\ Co(OH)_3 + 4\ NaCl + 2\ NaBr$$

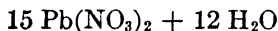
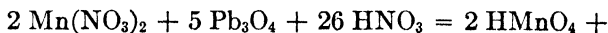
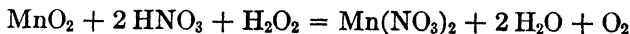
$$ZnCl_2 + 4\ NaOH = Na_2ZnO_2 + 2\ NaCl + 2\ H_2O$$

Filter and wash, reserving the precipitate to test for Mn. The filtrate is treated with 1–2 cc. of NH_4OH, boiled for a short time to reduce NaBrO (from excess Br_2),

$$Br_2 + 2\ NaOH = NaBrO + NaBr + H_2O$$

$$3\ NaBrO + 2\ NH_4OH = 3\ NaBr + N_2 + 5\ H_2O$$

then tested for Zn in one of the following ways: (a) pass in H_2S and look for a white precipitate of ZnS,

$$Na_2ZnO_2 + H_2S = ZnS + 2\ NaOH$$

or (b) acidify with $HC_2H_3O_2$ and either test with H_2S or add $K_4Fe(CN)_6$ and look for a white precipitate of $Zn_2Fe(CN)_6$.

$$Na_2ZnO_2 + 4\ HC_2H_3O_2 = Zn(C_2H_3O_2)_2 + 2\ NaC_2H_3O_2 + 2\ H_2O$$
$$2\ Zn(C_2H_3O_2)_2 + K_4Fe(CN)_6 = Zn_2Fe(CN)_6 + 4\ KC_2H_3O_2$$

To examine the above precipitate for Mn, wash thoroughly, dissolve in 5 cc. of HNO_3 containing 0.5 cc. of H_2O_2, place a test portion of 0.5–1 cc. in a test tube, add 5–10 cc. of HNO_3, plus 0.5–1 g. Pb_3O_4, boil for about 1 minute and let settle. If Mn is present the solution will be colored reddish purple due to $HMnO_4$.

$$MnO_2 + 2\ HNO_3 + H_2O_2 = Mn(NO_3)_2 + 2\ H_2O + O_2$$
$$2\ Mn(NO_3)_2 + 5\ Pb_3O_4 + 26\ HNO_3 = 2\ HMnO_4 + 15\ Pb(NO_3)_2 + 12\ H_2O$$

§143. Notes. — 1. It is necessary to remove the H_2S before treating with NaOH, otherwise ZnS would precipitate and might be lost.

2. Manganese dioxide is less soluble than $Mn(OH)_2$, therefore the use of an oxidizing agent with the NaOH gives a more complete separation of Mn from Zn than NaOH alone.

3. Cobaltous hydroxide is slightly soluble in NaOH, giving a blue solution. When considerable Mn is present so the Br_2 is used up without the Co being oxidized, the filtrate from MnO_2 is sometimes blue instead of colorless. In such a case add 3–5 cc. Br_2-water, shake and let stand a moment. The Co is thus oxidized and precipitated as $Co(OH)_3$. This may be filtered out and the filtrate then tested for Zn (after reduction of NaBrO).

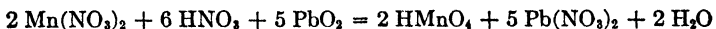
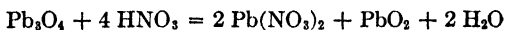
4. Failure to reduce NaBrO may result in the precipitation of S from the H_2S, which might be mistaken for ZnS. In such a case Zn might be tested for by treating the precipitate with HCl, filtering, neutralizing with NH_4OH, and reprecipitating with H_2S. ZnS dissolves in HCl but S does not.

5. The common ions of Zn are Zn^{++}, $Zn(NH_3)_4^{++}$ and $HZnO_2^-$. The first one is found only in neutral or acid solution, the latter two in alkaline solution. These two are distinguished from each other by the odor of the solution or the action of the vapors on litmus paper. If the solution is alkaline with NH_4OH, $Zn(NH_3)_4^{++}$ is present, if alkaline with "fixed alkali" (NaOH, KOH, etc.) $HZnO_2^-$ is present.

6. Cobalt and Ni do not interfere seriously with the test for Mn, although in the case of Co a light red solution is sometimes obtained that might be mistaken for a very dilute solution of MnO_4^-. A partial separation of Mn from Co and Ni may be accomplished by merely pouring the $HNO_3 + H_2O_2$ solution through the filter once. Manganese dioxide dissolves much more readily than either of the others, so the latter will be left behind largely by this treatment while sufficient MnO_2 will dissolve to give a satisfactory test.

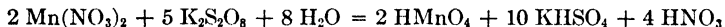
Another method which gives a more complete separation and recovers all of the Mn is as follows: Dissolve the precipitate completely in $HNO_3 + H_2O_2$, add 3–5 cc. NH_4Cl, plus 4–5 cc. excess of NH_4OH, then add 0.5 g. $K_2S_2O_8$ and boil 1–2 minutes. Manganese is reprecipitated as MnO_2 while Co and Ni stay in solution as complex ammonia salts. Filter, wash thoroughly, dissolve in $HNO_3 + H_2O_2$ and test for Mn.

7. The test for Mn frequently causes more trouble when Mn is present in large amounts than when in small amounts. This is due to failure to oxidize any of the Mn beyond the stage of MnO_2. This may result from not using sufficient Pb_3O_4 or from not using a corresponding excess of HNO_3, since part of the HNO_3 is used up by the Pb_3O_4, and excess of HNO_3 must be present in order that the Mn may be oxidized.

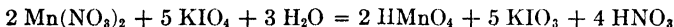
$$Pb_3O_4 + 4\ HNO_3 = 2\ Pb(NO_3)_2 + PbO_2 + 2\ H_2O$$
$$2\ Mn(NO_3)_2 + 6\ HNO_3 + 5\ PbO_2 = 2\ HMnO_4 + 5\ Pb(NO_3)_2 + 2\ H_2O$$

However, the test for Mn is unusually delicate, because of the high coloring power of MnO_4^-, so the above difficulty may be avoided by taking only a small portion of the

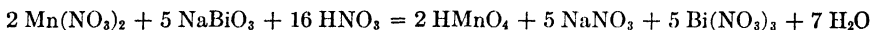
solution and adding moderate quantities of Pb_3O_4 and HNO_3. If the test fails on this portion it may be because the actual amount of Mn present is very small. In that case, try the test again using the remaining portion of the solution.

8. Another method of oxidizing Mn^{++} to MnO_4^- uses $K_2S_2O_8$ with $AgNO_3$ as catalyst. This works very well for small amounts of Mn but the upper limit for satisfactory oxidation is about 2 mg. in 10–15 cc. The precedure is as follows: To a test portion of the solution add 3–5 cc. of HNO_3, then add 0.5 cc. of $AgNO_3$. If a white precipitate of AgCl forms, shake, filter, and add a few drops more of $AgNO_3$. Add 1 g. of $K_2S_2O_8$, and heat to boiling. If Mn is present the usual reddish purple color will develop.

$$2\,Mn(NO_3)_2 + 5\,K_2S_2O_8 + 8\,H_2O = 2\,HMnO_4 + 10\,KHSO_4 + 4\,HNO_3$$

The $AgNO_3$ is oxidized to Ag_2O_2, but is reduced again in the process so does not appear in the equation. If too much $AgNO_3$ is used a black precipitate of Ag_2O_2 will form.

9. Potassium periodate, KIO_4, is a fairly expensive oxidizing agent that is being used with marked success for the colorimetric estimation of Mn. Oxidation proceeds directly to MnO_4^- (in HNO_3 or H_2SO_4 solution) and the solution is unusually stable. The solution must be boiled several minutes to oxidize the Mn.

$$2\,Mn(NO_3)_2 + 5\,KIO_4 + 3\,H_2O = 2\,HMnO_4 + 5\,KIO_3 + 4\,HNO_3$$

10. Sodium bismuthate, $NaBiO_3$, and BiO_2, are powerful oxidizing agents (also expensive), which oxidize Mn directly in the cold in moderately acid solution.

$$2\,Mn(NO_3)_2 + 5\,NaBiO_3 + 16\,HNO_3 = 2\,HMnO_4 + 5\,NaNO_3 + 5\,Bi(NO_3)_3 + 7\,H_2O$$

11. Manganese may be tested for fairly directly on the original solution if it is first treated with 1–2 cc. of concentrated H_2SO_4, evaporated to fumes of SO_3, cooled and diluted with water. This removes Cl^- and other reducing agents that would interfere with oxidation of the Mn.

12. The common ions of Mn are Mn^{++}, MnO_4^{--}, and MnO_4^-. The first is found in neutral or acid solution and is colorless; the second (manganate ion) is dark green in color and is stable only in strongly alkaline solution; on acidifying, it changes to MnO_4^- and MnO_2.

$$3\,K_2MnO_4 + 4\,HNO_3 = 2\,KMnO_4 + MnO_2 + 4\,KNO_3 + 2\,H_2O$$

Permanganate ion, MnO_4^-, is reddish purple and may be found in acid, neutral, or alkaline solution. Alkaline solutions containing NH_4OH reduce MnO_4^{--} and MnO_4^- to MnO_2.

$$2\,KMnO_4 + 2\,NH_4OH = 2\,MnO_2 + N_2 + 2\,KOH + 4\,H_2O$$

THE COMBINED PRECIPITATION OF GROUPS III AND IV BY $(NH_4)_2S$

§144. Many chemists prefer to avoid some of the difficulties of separation of Groups III and IV (as considered in this book) by precipitating all of these metals as a single group, which then becomes Group III in such a system. With proper care there is little to choose between the two schemes in the matter of accuracy, and the gain in simplicity of precipitation of the group may be largely offset by the greater complexity of analysis of the larger group.

The precipitation of the group in this case is carried out as follows: To the filtrate from Group II (without boiling out H_2S or oxidizing Fe^{++}) add 5–10 cc. of NH_4Cl, heat to boiling, add NH_4OH till alkaline, plus 5 cc. excess, then pass in H_2S for about 1 minute, filter and test with more H_2S for completeness of precipitation. The precipitate obtained will consist of

$Al(OH)_3$, $Cr(OH)_3$, and sulfides of the rest of the metals. The following outline for the analysis of the precipitate uses the same procedures as are involved in Groups III and IV and should be supplemented by corresponding notes:

Transfer the precipitate to a casserole, digest 1–2 minutes with 25 cc. of cold *N* HCl, filter and wash. Examine the precipitate for Co and Ni (§140, §141). Boil the filtrate to remove H_2S, neutralize with NaOH, adding 10 cc. excess, add 5–8 cc. H_2O_2, boil 1–2 minutes, filter and wash. Examine the precipitate for Fe and Mn (§130, §131, note 3), and the filtrate for Al, Cr and Zn (§130, §131, notes 3 and 16).

INTERFERENCE OF PHOSPHATES AND OXALATES IN THE SEPARATION OF GROUP III FROM LATER GROUPS

§145. The group separations described thus far have assumed that the solutions being analyzed contained nothing that would interfere with the proper precipitation of the individual groups or with a reasonably accurate separation of each group from later groups. It is possible, however, to introduce materials into the solution such that this simple condition will no longer exist. The presence of substances in the solution with which various of the metals combine to form stable complex ions may result in the failure of these metals to precipitate with the usual group reagent. Further, the presence in the solution of substances which, under certain conditions, form insoluble compounds with some of the later group metals may result in the formation of these precipitates when some of the earlier groups are being precipitated, in spite of the fact that the usual precautions have been observed in establishing the proper conditions for satisfactory separation of the groups. Thus, if the solution contained a considerable amount of acetic acid, the directions given in §80 (neutralizing with NH_4OH and adding 5 *N* HCl in the ratio of 1 part by volume of acid to 19 parts of the neutral solution) might still leave the solution with a low enough concentration of hydrogen ion so that several sulfides of Groups III and IV might precipitate along with Group II. Or if the solution contained a high concentration of citric, oxalic, or tartaric acid when attempting to precipitate Group III with NH_4OH, the hydroxides of Fe, Cr and Al might fail to precipitate even though these metals were present. In the case of oxalic acid, not only may the precipitation of Group III be hindered, but oxalates of several of the metals of Groups IV–VI will precipitate when the solution is neutralized with NH_4OH.

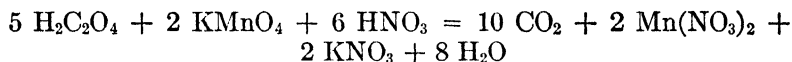
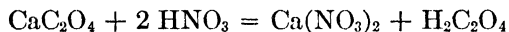
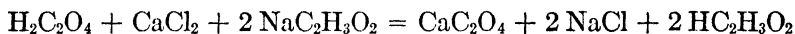
§146. Among the materials commonly included for qualitative examination, oxalic and phosphoric acids are the chief ones to cause trouble of the sort just mentioned. These do not interfere appreciably in the separation of Groups I and II from later groups because the first two groups are pre-

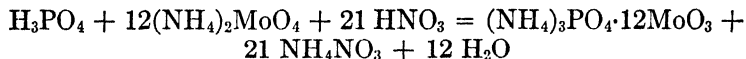
cipitated in the presence of sufficiently high concentration of hydrogen ion to prevent the formation of phosphates or oxalates of later group metals. But in making the solution alkaline for the precipitation of Group III the concentrations of oxalate and phosphate ions are considerably increased. Since most of the metals of Groups IV and V (including Mg) form insoluble phosphates and oxalates, it is clear that the precipitation of Group III with ammonium hydroxide will not separate Fe, Cr and Al from these other metals. Therefore in dealing with unknowns in which these materials may be present, it becomes necessary to examine the filtrate from Group II for such interfering substances, and, if they are present, to take adequate steps to remove them or to avoid their interference.

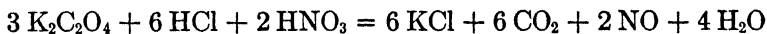
To test for oxalate and phosphate, the filtrate from Group II is first boiled as usual to remove H_2S. A portion of the solution may then be used to *test for oxalate.* To 2–3 cc. of the solution add 1–2 cc. of $CaCl_2$, then 2–3 cc. of $NaC_2H_3O_2$ solution. If a precipitate forms, filter and wash thoroughly, then transfer the precipitate to the casserole. Add 5 cc. of 5 *N* HNO_3, heat to boiling, add 3–5 cc. of H_2O and boil gently for 2–3 minutes. Let cool slightly (the casserole should still feel rather hot on the bottom), then add a drop or two of very dilute $KMnO_4$ solution (0.04 – 0.1 *N*). If the permanganate color disappears, an oxalate is present.

$$H_2C_2O_4 + CaCl_2 + 2\,NaC_2H_3O_2 = CaC_2O_4 + 2\,NaCl + 2\,HC_2H_3O_2$$

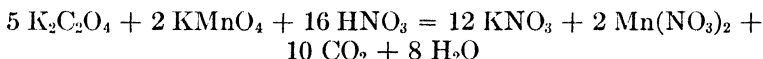
$$CaC_2O_4 + 2\,HNO_3 = Ca(NO_3)_2 + H_2C_2O_4$$

$$5\,H_2C_2O_4 + 2\,KMnO_4 + 6\,HNO_3 = 10\,CO_2 + 2\,Mn(NO_3)_2 + 2\,KNO_3 + 8\,H_2O$$

A second portion of the solution is used to *test for phosphate.* To 2–3 cc. of the solution add 2–3 cc. of HNO_3, boil to oxidize any Fe^{++}, then add 5–10 cc. of $(NH_4)_2MoO_4$, and warm gently. If a bright yellow precipitate forms, a phosphate is present.

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21\,HNO_3 = (NH_4)_3PO_4\cdot 12MoO_3 + 21\,NH_4NO_3 + 12\,H_2O$$

§147. The two methods commonly used to remove oxalate are (a) to add 10–15 cc. of HNO_3 to the solution, evaporate to dryness in a casserole, and heat the dry residue strongly, or (b) to add 15–20 cc. of nitro-hydrochloric acid, heat to boiling, and let evaporate slowly approximately to dryness, regulating the flame so that the solution will be kept at the boiling point for 25–30 minutes.

$$3\,K_2C_2O_4 + 6\,HCl + 2\,HNO_3 = 6\,KCl + 6\,CO_2 + 2\,NO + 4\,H_2O$$

If other organic acids (or organic matter in general) may be present, the first method is preferred, for these are all decomposed by this treatment.

If only oxalic acid is to be removed, the second method is the better, because of the difficulty usually encountered in dissolving with 5 *N* HCl the basic salts and oxides formed in the first method from decomposition of the nitrates of certain metals of Groups III and IV. In either case, it is desirable to make certain that the oxalate has been completely removed by repeating the test for oxalate. If it is still present, repeat the operation with closer attention to the details indicated above. A third method, occasionally used for the removal of oxalate radical, consists in adding 5–10 cc. of HNO_3 to the filtrate from Group II (after removal of H_2S), warming to 60°, and adding $KMnO_4$ solution carefully until it is no longer decolorized promptly.

$$5\ K_2C_2O_4 + 2\ KMnO_4 + 16\ HNO_3 = 12\ KNO_3 + 2\ Mn(NO_3)_2 + 10\ CO_2 + 8\ H_2O$$

This oxidizes the oxalate to CO_2 and is very simple and rapid to carry out. The only disadvantages are that it introduces K and Mn, so that tests for these must be made on another portion of the original solution, and, further, MnS will precipitate in Group IV even though no Group IV metals are present in the original solution. In this procedure, following the oxidation of the oxalate, a few drops of formaldehyde are added to reduce any excess of $KMnO_4$. The solution is boiled for a short time, and is then ready to treat with NH_4Cl and NH_4OH as usual for the precipitation of Group III.

§**148**. The removal of phosphate is less direct than the removal of an oxalate. No reagents can be added to decompose it, or to oxidize or reduce it to some volatile form. The only procedures left are precipitation processes, by which it may be removed, or by which satisfactory separations may be carried out in spite of its presence. Five of these will be discussed briefly, under the names, (*a*) the metallic tin method, (*b*) the stannic chloride method, (*c*) the basic acetate method, (*d*) the ferric chloride method, and (*e*) the sodium carbonate method.

(*a*) *The metallic tin method.* — Add to the solution 10–15 cc. of HNO_3 and evaporate to dryness to remove chlorides. Dissolve the residue in about 15 cc. of 5 *N* HNO_3, add 1 g. of metallic tin, heat until the reaction of the tin with the nitric acid is fairly vigorous, and continue until the tin has been fully converted to the white precipitate of stannic acid. Boil for a few minutes, let the precipitate settle, then filter. Test the filtrate again for phosphate. If still present, add more HNO_3 and Sn and repeat. The stannic acid formed by the action of nitric acid on the tin adsorbs moderate amounts of phosphate (possibly as stannic phosphate, $Sn_3(PO_4)_4$). If the quantity of phosphate present is small it may be completely removed in a single operation, but with larger quantities (over

0.025 g.) the process may need to be repeated several times. Further, metallic tin occasionally contains small amounts of lead, copper and iron as impurities. Therefore, after removal of phosphate, a procedure should be introduced to get rid of any Cu and Pb (precipitation with H_2S in slightly acid solution); and allowance must be made for any Fe introduced from the tin.

(*b*) *The stannic chloride method.* — Gattermann and Schindhelm[1] found that a freshly prepared solution of $SnCl_4$ was much more effective in removing phosphate radical from solution than the stannic acid as formed in (*a*). In fact, the readiness with which fairly large amounts of phosphate can be removed makes it seem reasonable to consider that the reaction involved is precipitation of the phosphate as stannic phosphate, $Sn_3(PO_4)_4$, rather than adsorption of phosphate ion by the colloidal stannic acid. With a small amount of phosphate present the precipitate is hard to filter, but with larger amounts no difficulty is encountered. Therefore, if the original test for phosphate showed only a moderate amount present, it may be desirable to add more to the solution before attempting the precipitation. For this purpose a solution of $(NH_4)_2HPO_4$ should be available, containing 6 g. in 100 cc., 5 cc. of this solution being ample to take care of the difficulty mentioned. The reagent, $SnCl_4$, is a freshly prepared solution of 5 g. of the crystallized salt in 5 cc. of cold water. The reagent should be prepared immediately before use. On standing it slowly loses its effectiveness although the solution suffers no visible change. The directions as worked out by the above authors are as follows:

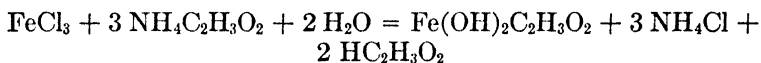
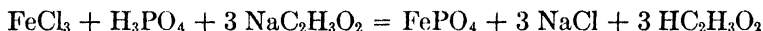
Boil the filtrate from Group II to remove H_2S, dilute with water to 100 cc., add 5 cc. $(NH_4)_2HPO_4$ solution (if necessary), add NH_4OH carefully until the precipitate which forms will barely redissolve on shaking, then add 1.5 cc. of 5 *N* HCl. Heat again to boiling, add 3 cc. of the $SnCl_4$ solution, filter 2–3 cc. of the solution and test for PO_4^{-3} with $(NH_4)_2MoO_4$. If test is positive, add 1 cc. more of the $SnCl_4$ solution and repeat; continuing as necessary until the test for PO_4^{-3} is negative. Filter and wash, discarding the precipitate. To the filtrate add 3 cc. of 5 *N* HCl, precipitate the Sn with H_2S, filter, discard the precipitate, and analyze the filtrate as usual for Groups III–VI.

(*c*) *The basic acetate method.* — This method depends upon the fact that $FePO_4$ is insoluble in dilute acetic acid while the phosphates of the later group metals are appreciably soluble in this reagent, and further, if a solution of ferric acetate is diluted largely with water and boiled the iron is precipitated quantitatively as a basic acetate $[Fe(OH)_2C_2H_3O_2 - Fe_2(OH)_5C_2H_3O_2]$. If Al^{+3} and Cr^{+3} are present they will be precipitated with reasonable completeness at the same time. This makes it possible to precipitate Group III as basic acetates with removal of PO_4^{-3} at the same time as $FePO_4$. The procedure is as follows:

[1] Gattermann and Schindhelm, *Ber.*, **49**, 2416 (1916).

Boil the filtrate from Group II to remove H_2S, and oxidize any Fe^{++} with HNO_3. Then add NH_4OH carefully, with shaking, until the precipitate that forms just fails to redissolve. Then add 2–3 cc. of 5 *N* $HC_2H_3O_2$ and 10–15 cc. of 3 *N* $NH_4C_2H_3O_2$, and note the color of the solution. If the solution contains more than enough Fe^{+3} to be equivalent to the PO_4^{-3} present, it will be red in color, due to colloidal $Fe(OH)_3$ or $Fe(OH)_2C_2H_3O_2$ in suspension. If the solution is not red in color, add $FeCl_3$ solution until a definite color develops (similar to $Fe(OH)_3$ but possibly modified by the presence of other colored ions in the solution). Then dilute with water to at least 100 cc., boil for 3–5 minutes, filter, and wash the precipitate with hot water. The precipitate may be analyzed as usual for Group III (if $FeCl_3$ was added special tests for Fe should be applied to the original solution). The filtrate is examined as usual for Groups IV–VI.

$$FeCl_3 + H_3PO_4 + 3\,NaC_2H_3O_2 = FePO_4 + 3\,NaCl + 3\,HC_2H_3O_2$$

$$FeCl_3 + 3\,NH_4C_2H_3O_2 + 2\,H_2O = Fe(OH)_2C_2H_3O_2 + 3\,NH_4Cl + 2\,HC_2H_3O_2$$

(*d*) *The ferric chloride method.* — This method employs some of the reactions involved in the basic acetate procedure; namely, the insolubility of the Group III phosphates in dilute $HC_2H_3O_2$ as compared with the appreciable solubility of the later group phosphates. It proposes the precipitation of Group III as phosphates in acetic acid solution, followed by removal of excess PO_4^{-3} as $FePO_4$ in the filtrate. The Group III precipitate is analyzed in the usual way, the PO_4^{-3} not interfering with the ordinary separations and tests (except that the confirmatory test for Al by the "Aluminon reagent" may not work). The details of the procedure are as follows:

After removal of H_2S and oxidation of Fe^{++} in the filtrate from Group II, the solution is treated with NH_4OH until a precipitate barely persists after shaking. Add 2–3 cc. of 5 *N* $HC_2H_3O_2$ and 3–5 cc. of 3 *N* $NH_4C_2H_3O_2$, then treat with $(NH_4)_2HPO_4$ in small amounts at a time until precipitation appears to be complete. Filter and test the filtrate with a few more drops of the reagent. Wash the precipitate and test it as usual for Group III. To the filtrate add 5–10 cc. more of 3 *N* $NH_4C_2H_3O_2$, then add $FeCl_3$ solution (specially prepared by dissolving the salt in water without using free HCl, then filtering or decanting the clear solution), a few drops at a time, with shaking, until the first reddish tinge appears, indicating that the PO_4^{-3} is completely precipitated as $FePO_4$ and a slight excess of Fe^{+3} has changed to colloidal $Fe(OH)_2C_2H_3O_2$. Filter and discard the precipitate. Heat the filtrate, add a slight excess of NH_4OH to precipitate the Fe and the small amount of Cr that may have escaped precipitation as $CrPO_4$, and filter. If Cr was not identified earlier, wash this precipitate

and test it for Cr, otherwise discard the precipitate and use the filtrate to test for the metals of Groups IV–VI.

(e) *The sodium carbonate method.* — In this method Group III is precipitated in the usual way with NH_4OH, without attempting to remove PO_4^{-3} first. The precipitate is then treated in such a way as to convert the later group metals to carbonates, leaving PO_4^{-3} in solution. The precipitate is filtered out and analyzed for Group III and later group metals, the filtrate being discarded. The procedure is as follows:

Precipitate Group III as usual with slight excess of NH_4OH in a hot solution containing a high concentration of NH_4Cl. Filter and wash thoroughly. The filtrate is analyzed for Groups IV–VI. Transfer the precipitate to a beaker or casserole, add 3–5 cc. of 5 N HCl, and heat as necessary to dissolve the precipitate. Then add 15–20 cc. of 5 N Na_2CO_3, heat to boiling and let digest hot for 5–10 minutes. Filter and wash. The filtrate, containing the PO_4^{-3} and excess carbonate may be discarded (a small amount of Al may be present in the form of AlO_2^- for which a test may be applied). The precipitate, consisting of hydroxides of the Group III metals and carbonates of such later group metals as were precipitated as phosphates in Group III, is dissolved in dilute HCl. Boil to remove CO_2, then add NH_4Cl and NH_4OH to precipitate Group III, examining the precipitate for Fe, Cr and Al, and testing the filtrate in the regular way for such metals of later groups as may be present.

§**149**. Oxalate and phosphate radicals are not the only ones that may cause interference in the analysis of Groups III–VI. The general specifications of such an interfering acid radical are these:

(1) it must be derived from a weak acid,

(2) it must form salts with some of the later group metals insoluble in dilute NH_4OH,

(3) these salts must be soluble in HCl, the products remaining in solution,

(4) it must not be removed or destroyed by reactions employed in the regular or special procedures used in precipitating Groups I–II.

§**150**. An examination of the list of ordinary acid radicals in the light of these specifications shows that relatively few will cause trouble. This will be apparent in the following brief discussion of the more obvious cases. Failure to remove arsenic completely may result in the precipitation of arsenites or arsenates of certain of the later group metals in Group III. Dichromate ion might interfere, but it is reduced at the beginning of Group II, or, if one is starting the analysis with Group III, is reduced as a first step before precipitation with NH_4OH. Sulfite ion might interfere if one omitted the precipitation of Group II, but the H_2S in Group II would reduce any H_2SO_3 to S°, thus destroying the sulfurous acid.

§151. The only other common acid radical that needs to be considered is the borate. This will interfere in the same way as a phosphate, and needs special attention if present. However, boron fluoride, BF_3, is sufficiently volatile that it may be removed by evaporation with HF or a mixture of HF and H_2SO_4. If H_2SO_4 is objectionable, due to the precipitation of insoluble sulfates, the other alternative is to add excess of HCl, evaporate barely to dryness, then add 25 cc. of methyl alcohol and again evaporate to dryness. Moisten the residue again with concentrated HCl, add more alcohol, and evaporate again. The boron is slowly volatilized in this procedure as methyl borate, $(CH_3)_3BO_3$.

THE RARER METALS OF THE IRON AND ZINC GROUPS

BERYLLIUM, CERIUM, COLUMBIUM, DYSPROSIUM, ERBIUM, EUROPIUM, GADOLINIUM, GALLIUM, HAFNIUM, HOLMIUM, ILLINIUM, INDIUM, LANTHANUM, LUTECIUM, NEODYMIUM, PRASEODYMIUM, SAMARIUM, SCANDIUM, TANTALUM, TERBIUM, THORIUM, THULIUM, TITANIUM, URANIUM, VANADIUM, YTTERBIUM, YTTRIUM, ZIRCONIUM.

The rarer metals of Groups III and IV have been so designated, to a certain extent at least, because of lack of knowledge regarding their qualitative (and quantitative) differentiation. As analysts become more familiar with these elements, the term "rarer" loses its significance. A few years ago, titanium was deemed quite uncommon, whereas now it is known that practically all silicate rocks contain a small amount, less than 1% on the average, but sufficient to rank the element as ninth in actual abundance in the earth's crust.[1] Down to 1922 it was unknown that practically all zirconium tests previously made were open to question because of the possible presence of hafnium. Yet, despite the large amount of research work during the last two or three decades, the analyst still lacks satisfactory methods for separation of the rarer elements. This is especially true regarding the 16 of atomic numbers 57 to 72 inclusive[2] (see Table 36), known as the rare earths. Precipitated before or with Group III, these metals are either ignored completely, or, if necessary separated from Fe, etc., and by means of fractional crystallization[3] roughly divided into two sub-groups, the cerium earths and the yttrium earths.[4] The difficulty, of course, is the similarity in properties or, what amounts to the same statement, the lack of sharply differentiating reactions. No attempt, therefore, will be made here to consider each rare earth element in detail.

[1] Clarke and Washington, U. S. Geol. Survey, Professional Paper 127, p. 20 (**1924**).

[2] Scandium (No. 21) and Yttrium (No. 39) are usually included, bringing the total to 18.

[3] One recorded attempt to separate a mixture into pure components involved 15,000 fractionations.

[4] The division is by no means sharp: cf., Noyes and Bray, p. 149 and 209, for a different grouping.

§154. Beryllium[1, 2] (L. *beryl*). Be = 9.02. Atomic No. 4. Valence 2. Discovered[3] by Vauquelin in 1797; isolated by Wöhler in 1828.

1. Physical Properties. — Density, 1.842 at 18°;[4] melting point, 1370° (purity of sample = 99.6%[5, 6]). Beryllium is a silvery white metal, malleable, almost as hard as quartz, only superficially attacked by air. It has an electrical conductivity higher than copper. Apparently the only present use for pure Be° is as a window in X-ray tubes in place of Al° which is many times more opaque. Alloys with Al, Cu, etc., have been studied to some extent. They are said to offer interesting possibilities provided the metal can be obtained in commercial quantities at a reasonable price. The substitution of Be° for some of the CaO in glass is said to increase its hardness and melting point.

2. Occurrence. — Beryl, $Be_3Al_2(SiO_3)_6$, containing 11%–13% BeO, is the most important beryllium mineral. The opaque form is occasionally found as very large crystals — over 25 ft. long and weighing as much as a ton — in the New England states. Other localities are: South Dakota and Colorado in the United States, South Africa, Madagascar, Austria, France, etc. Beryl of gem quality, especially the emerald, is found chiefly in Colombia, South America.[7] At present two grades of ore are sold, one averaging 6%–8%, the other 10%–12% of BeO. The total production amounts to only a few hundred tons and commands a price of $25–$30 per ton for the higher grade.[8]

3. Preparation. — In the United States the process used is electrolysis of fused $BeCl_2$ at about 700°, i.e., below the melting point of the metal. The product thus obtained is in the form of flakes. In Germany a method similar to that employed for the metallurgy of aluminum is in operation. Beryllium oxyfluoride, mixed with BaF_2, is electrolyzed at 1300°–1400°. The metal thus secured has a purity of 99.5% or higher.[9]

4. Oxide and Hydroxide. — Beryllium oxide, BeO, white, is prepared by ignition of Be°, $Be(OH)_2$ and certain of the salts as the nitrate, sulfate and basic carbonate. It is said to be as good as magnesia for refractory purposes. Beryllium hydroxide, $Be(OH)_2$, is precipitated by NH_4OH from solutions of Be^{++}. The gelatinous product is amphoteric and closely resembles $Al(OH)_3$ in many of its properties.

5. Solubilities. — Beryllium is but slightly affected by H_2O, or cold HNO_3; readily soluble in NaOH, HCl, hot HNO_3,[10] and in dilute H_2SO_4 with evolution of H_2. If the acid is hot and concentrated SO_2 is evolved. Beryllium oxide is insoluble in H_2O; readily soluble in acids and alkali hydroxides (ignition decreases the solubility).[11] Beryllium hydroxide is insoluble in H_2O and NH_4OH, readily soluble in acids and the fixed alkalis except that standing decreases the rate of solution in the latter solvents. The halide salts are deliquescent, the basic carbonate slightly soluble in H_2O, the double fluorides, e.g., $BeF_2 \cdot 2NaF$, moderately soluble.

[1] Also called Glucinum.

[2] Hoyt and v.d. Steinen, *Quart. Colo. School of Mines*, **26**, No. 4, 3–35 (1931), give a good bibliography.

[3] Cf. Marchal, *Chimie & industrie*, **22**, 1084–92 (1929); **23**, 30–3 (1930), *C.A.* **24**, 1559.

[4] Stock, *et al.*, *Ber.*, **58B**, 1571 (1925).

[5] Hunter and Jones, *Trans. Am. Electroch. Soc.*, **44**, 26 (1923).

[6] For a review of the literature on the physical properties of Be see: Illig, *Wiss. Veröff. Siemens-Konzern* [1] **8**, 74–82 (1929), *C.A.* **24**, 1810.

[7] Cf. Gmelin, 8th ed., No. 26 (1930), p. 5–15.

[8] Mineral Ind., **1929**, p. 690.

[9] *Idem.*, cf., Dyson, *Ch. Age (London)*, **24**, 228–30 (1931), *C.A.* **25**, 2066. Illig, *Wiss. Veröff. Siemens-Konzern*, [1] **8**, 30–58 (1929), *C.A.* **24**, 2379. Vivian, *Trans. Faraday Soc.*, **22**, 211 (1926).

[10] Bodforss, *Z. physik. Ch.*, **124**, 68 (1926).

[11] Fischer, *Wiss. Veröff. Siemens-Konzern*, [1] **8**, 9–20 (1929), states that strongly ignited BeO is insoluble in all acids except HF.

6. Reactions. — In many respects Be^{++} is closely related to the ions of alkaline earth metals, particularly Mg^{++}, as would be inferred from its position in the periodic system. It is, however, precipitated as the hydroxide, $Be(OH)_2$, by NH_4OH or the fixed alkalis and is readily soluble in excess of the latter, which properties justify the usual analytical classification with Al^{+3}. An important difference is that on boiling a solution of beryllate, BeO_2^{-}, a precipitate of $Be(OH)_2$ is readily obtained whereas AlO_2^{-} is not affected. Solutions of the alkali carbonates precipitate Be^{++} as the basic carbonate[1] soluble in excess of the reagent when freshly precipitated.[2] Oxalic acid or $(NH_4)_2C_2O_4$ forms no precipitate with Be^{++}. Ammonium sulfide precipitates Be^{++} as $Be(OH)_2$. Soluble sulfates precipitate, from solutions sufficiently concentrated, a crystalline precipitate of beryllium sulfate[3] (distinction from Ce, La, Nd, Pr). Ammonium phosphate precipitates Be^{++} from neutral or slightly acid solutions as $BeNH_4PO_4$ which upon ignition is converted to $Be_2P_2O_7$.

7. Ignition. — Fusion of BeO with Na_2CO_3 does not affect the oxide; fusion with Na_2SiF_6, however, results in the formation of moderately soluble Na_2BeF_4.

8. Detection. — *a.* Beryllium is precipitated as $Be(OH)_2$, along with $Al(OH)_3$, the precipitate dissolved in only a slight excess of 5 *N* NaOH and the solution boiled[4] whereupon $Be(OH)_2$ reprecipitates and may be identified by reactions given above.

b. The aluminon reagent (ammonium salt of aurintricarboxylic acid) forms a red lake with Be^{++} the same as Al^{+3}. Diphenylcarbazide in dilute alcohol forms a deeply colored solution with $Be(OH)_2$.[5] Quinalizarin added to a slightly alkaline beryllium solution gives a cornflower blue lake. The reagents alone produce a violet color[6] (Fe, Mg, phosphates and tartrates interfere, Al does not). Curcumin is adsorbed by $Be(OH)_2$ with the formation of an orange-red color.[7] Fe and Al interfere; Mg lowers the sensitivity of the test.

9. Determination. — *Gravimetrically,* Be^{++} may be precipitated as the hydroxide, ignited and weighed as BeO[8, 9].

§156. The Rare Earth Metals

Cerium Sub-group (Potassium sulfates insoluble to slightly soluble)	Scandium Lanthanum Cerium Praseodymium Neodymium Illinium Samarium Europium Gadolinium	*Yttrium Sub-group* (Potassium sulfates moderately to readily soluble)	Terbium Dysprosium Holmium Erbium Thulium Ytterbium Lutecium (Hafnium) Yttrium

1. Physical Properties. — See Table 36.

2. Occurrence. — Minerals containing the rare earths number about 150 and are widely scattered. Individual deposits, however, are small and usually mixed with other

[1] Cf. Nishimura and Yamamoto, *Bull. Inst. Phys. Ch. Research (Tokyo)*, **7**, 920–33 (1928); English Ed., **1**, 89–90, *C.A.* **23**, 351.

[2] Bleyer and Boshart, *Z. anal. Ch.*, **51**, 748 (1912).

[3] Taboury, *Compt. rend.*, **154**, 180 (1914).

[4] $Be(OH)_2$ is soluble in a saturated solution of $NaHCO_3$, $Al(OH)_3$ insoluble.

[5] Feigl, *Ber. Wien. Akad.*, **133**, 121 (1924).

[6] Fischer, *Wiss. Veröff. Siemens-Konzern,* [1] **2**, 99 (1926). He also gives a fairly complete account of methods for the detection and determination of Be. Cf. *Z. anal. Ch.*, **73**, 54 (1928).

[7] Kolthoff, *J. Am. Ch. Soc.*, **50**, 393 (1928). Cf. Thrun, *Ind. Eng. Ch., Anal. Ed.*, **2**, 8–9 (1930).

[8] Hillebrand and Lundell, p. 407, say that beryllium cannot be precipitated as the phosphate and weighed as the pyrophosphate.

[9] For the separation of Be from other cations see: Moser and Brandl, *Monatsh.*, **51**, 181 (1929), *C.A.* **23**, 2387.

TABLE 37

Some Properties of the Rare Earth Metals

Name	Source of Name	Symbol	At. Wt.	At. No.	Valence	Discovery	Density	M. Pt.	B. Pt.	Oxides	Hydroxides	Color of Salts
Scandium	Scandinavia	Sc	45.10	21	3	Nilson — 1879	(2.5)	1200°	2400°	Sc_2O_3 (white)	$Sc(OH)_3$	Colorless
Yttrium	Ytterby, a town in Sweden	Y	88.92	39	3	Mosander — 1842	4.57	1500°	2500°	Y_2O_3 (white)	$Y(OH)_3$	Colorless
Lanthanum	Gr. *lanthano* = to conceal	La	138.90	57	3	Mosander — 1837	6 15	826°	1800°	La_2O_3 (white)	$La(OH)_3$ (white)	Colorless
Cerium	Planet *Ceres*	Ce	140.13	58	3-4	Berzelius and Hisinger — 1803	6 8	640°	1400°	Ce_2O_3 (white) CeO_2 (white)	$Ce(OH)_3$ (white) $Ce(OH)_4$ (yellow)	-ous colorless -ic yellow
Praseodymium	Gr. *praseos didymos* = green twin	Pr	140.92	59	3	Welsbach — 1885	6.6	940°		Pr_2O_3 (green yellow) PrO_2(d. brown)	$Pr(OH)_3$ (green)	Green (salts?)
Neodymium	Gr. *neos didymos* new twin	Nd	144.27	60	3	Welsbach — 1885	7.0	840°		Nd_2O_3 blue) NdO_2 (blue)	$Nd(OH)_3$ (blue)	Rose red
Illinium	Univ. of *Illinois*	Il	*ca.* 146	61	3	Hopkins — 1926				Il_2O_3		
Samarium	Samarski = a Russian	Sm	150.43	62	3	Boisbaudran — 1879	7.7	>1300°		Sa_2O_3 (pale yellow)	$Sa(OH)_3$ (pale yellow)	Pink
Europium	Europe	Eu	152.00	63	3	Demarçay — 1906				Eu_2O_3		Rose
Gadolinium	Professor Gadolin	Gd	157.26	64	3	Marignac — 1886				Gd_2O_3		Colorless
Terbium	Ytterby, a town in Sweden	Tb	159.2	65	3	Mosander — 1842 (Delafontaine—1887)				Tb_2O_3 (white)		Colorless
Dysprosium	Gr. = hard to speak with	Dy	162.46	66	3	Boisbaudran — 1886				Dy_2O_3		Yellow
Holmium	Stockholm	Ho	163.5	67	3	Cleve — 1879				Ho_2O_3		Yellow
Erbium	Ytterby, a town in Sweden	Er	167.64	68	3	Mosander — 1842				Er_2O_3		Red
Thulium	*Thule* = Northland	Tm	169.4	69	3	Cleve — 1879				Tm_2O_3		Green
Ytterbium	Ytterby, a town in Sweden	Yb	173.5	70	3	Urbain* — 1907				Yb_2O_3		Colorless
Lutecium	*Lutetia* = old name for Paris	Lu	175.0	71	3	Urbain — 1907				Lu_2O_3		Colorless
Hafnium	*Kobenhavn*, i.e., Copenhagen	Hf	178.6	72	4 (?)	Coster and Hevesy — 1922		1700°	>3200°	HfO_2		

* See Mellor, V, 705.

materials. Among the more important ores[1] are: gadolinite, a silicate of Fe, Be and the yttrium group, averaging 35%–48% yttria; cerite, a basic silicate of Ca and Fe, with cerium and yttrium earths, containing 50%–70% ceria and up to 8% yttria; xenotime, a phosphate of Th and Zr, with cerium and yttrium earths, 54%–65% yttria; euxenite, a columbate, containing Ti, U and Th, along with yttrium and cerium earths, yttria 13%–35%, ceria 2%–8%; fergusonite, an yttrium tantalo-columbate, carrying 28%–47% yttria and up to 13% ceria; samarskite, also a tantalo-columbate, but containing about half as much yttria and ceria as fergusonite; monazite, a cerium phosphate, 50%–75% ceria and up to 8% yttria; allanite, a hydrated silicate, containing up to 50% ceria and up to 8% yttria; yttrocerite, a fluoride of Y, Ce and Ca, 9%–18% ceria, 8%–29% yttria. Deposits of these ores are found in Greenland, Colorado, the Carolinas, Brazil, Peru, Scandinavia, the Ural Mountains, India, Australia, etc. While yttrium is the most abundant of that family, any one of the cerium sub-groups — excluding Sm — is more plentiful than yttrium. Incidentally, minerals high in yttria are more abundant than those rich in ceria.

The production of rare earths on a commercial scale is limited to cerium,[2] a by-product of the gas mantle industry. The only uses for cerium are: in gas mantles; as a component of the pyrophoric alloy[3] on cigarette lighters; for coloring ceramic ware; and in " carbons " for arc lights. In 1929 metallic Ce sold for about $5 per pound.

3. Preparation. — In some cases fairly pure metals have been prepared by electrolytic reduction of the oxide in a molten fluoride bath. Pure metallic Ce, La, Pr, Nd and Sm have been prepared by electrolysis of their fused chlorides in graphite cells.[4] Due, however, to the difficulty of separating these elements, and their highly electropositive nature, the task is by no means easy. The fact that so few of them have been isolated thus far is ample proof of the situation.

4. Oxides and Hydroxides. — See Table 36.

5. Solubilities. — *a.* In so far as known, the metals are all attacked by moist air; are insoluble in NaOH or NH_4OH; slowly react with H_2O, liberating H_2; and are readily soluble in acids.[5]

b. The oxides and hydroxides are soluble in acids, insoluble in the alkali hydroxides. The cerite earth hydroxides are somewhat soluble in H_2O,[6] the yttria group hydroxides, less soluble.

c. Carbonates of both groups are insoluble in H_2O; those of the yttrium group are fairly soluble in $(NH_4)_2CO_3$. The same applies to the oxalates. The fluorides and phosphates are insoluble in H_2O. The double sulfates of both groups vary from insoluble to readily soluble in a saturated solution of K_2SO_4 or Na_2SO_4, the sodium salts being in general somewhat more soluble. Nitrates of both groups are soluble in H_2O, basic nitrates are distinctly less soluble.

6. Reactions. — Solutions of the alkali hydroxides precipitate positive ions of the rare earth metals as $M(OH)_3$ (Ce^{+4} gives $Ce(OH)_4$, gelatinous), insoluble in excess of the reagent. If insufficient reagent is added, a basic salt may be obtained. Reaction in a cold medium gives a slimy product, difficult to filter or wash. The presence of ammonium acetate delays precipitation. The presence of citrate or tartrate ions prevents precipitation, except that in certain cases boiling promotes the separation of a complex tartrate, e.g., ammonium yttrium tartrate. All cerite hydroxides are strong bases although slightly soluble. $La(OH)_3$ approaches $Ca(OH)_2$ in basic strength. It will liberate NH_3 from solutions of ammonium salts.

Carbonates of the alkali metals precipitate normal or basic carbonates of the rare earths. The yttrium earth carbonates are soluble in excess of $(NH_4)_2CO_3$. Barium carbonate gives no precipitate with the yttrium earth ions in the cold and only partial

[1] Hopkins, p. 97.

[2] Contaminated with its close relatives.

[3] So-called "misch metal," containing 70% Ce, some Fe, Co and Ni. It gives off sparks if scratched.

[4] Schumacher and Harris, *J. Am. Ch. Soc.*, **48**, 3108 (1926). For yttrium see: Kremers, *et al.*, *Trans. Am. Electroch. Soc.*, **49**, 161 (1926).

[5] Except concentrated H_2SO_4.

[6] $La(OH)_3$ is sufficiently soluble to produce a solution alkaline to litmus.

precipitation in hot solution (distinction from Al, Th and the cerite group). Oxalic acid and normal oxalates precipitate oxalates of the rare earths, practically insoluble in $H_2C_2O_4$, slightly soluble in $(NH_4)_2C_2O_4$. Phosphoric acid and soluble phosphates precipitate rare earth phosphates — $CePO_4 \cdot 2H_2O$, etc. Hydrogen sulfide does not react with ions of the rare earths, except to reduce Ce^{+4}. Alkali sulfides precipitate the corresponding hydroxide. Potassium, sodium, or ammonium sulfate precipitates crystalline double salts of the cerite earths, slightly soluble in cold, moderately soluble in hot H_2O, almost insoluble in a saturated solution of the alkali sulfate. The yttrium earth sulfates are soluble under the conditions just mentioned. Hydrofluric acid and soluble fluorides precipitate ions of the rare earths as fluorides, slightly soluble in H_2O, insoluble in solutions of the alkali fluorides, but appreciably soluble in hot mineral acids. Lanthanum hydroxide, $La(OH)_3$, adsorbs iodine like starch. The blue color disappears on addition of an acid or a base. Iodic acid, HIO_3, precipitates iodates, readily soluble in HNO_3 except that $Ce(IO_3)_4$ is only slightly soluble.

7. Ignition. — In general, ignition of the metals and salts produces the oxide, M_2O_3. Cerium is definitely known to form a higher oxide, e.g., ignition of cerous oxalate yields CeO_2. Higher oxides of other cerite earths have also been reported.[1] Praseodymium nitrate fused with KNO_3 at 450° is said to yield PrO_2, a very powerful oxidizing agent.

8. Detection. — There is no simple method for the separation and identification of the individual rare earth elements when present in a mixture. It is barely possible, however, that the magnetic moment method, used recently by Allison[2] for another purpose, may become a powerful tool in this field. Meanwhile there are available several methods for the separation of the rare earths as a group and for a partial and rough subdivision within the group. (1) After the removal of Group II and excess H_2S, the solution is heated to boiling and treated with hot $H_2C_2O_4$. The precipitate is washed, ignited, and dissolved in a minimum of acid. Any Ce^{+4} is reduced, then the solution is saturated with K_2SO_4 and allowed to stand over night. The precipitate formed consists of the potassium sulfates of the cerite earths; the filtrate contains the yttrium subgroup. Further separations may be made by fractionation.[3] (2) The rare earths may be precipitated by NH_4OH, along with Fe, Cr and Al in Group III. The precipitate is dissolved and treated with $H_2C_2O_4$, etc., as above. This procedure avoids contaminating the solution to be tested for later groups. (3) Noyes and Bray[4] separate the rare earths along with indium and thorium as fluorides. Indium is removed as In_2S_3. Tetravalent thorium and cerium are precipitated as iodates, then separated by reduction of the cerium to Ce^{+3}, in which form the iodate is soluble. The metals remaining are partially divided into the cerium and yttrium sub-groups by treatment with K_2CO_3.

Identification of the rare earth elements after separation is, in certain cases, not difficult. The development of a yellow color due to the oxidation of Ce^{+3} to Ce^{+4} by means of $NH_4OH + H_2O_2$ is said to make possible the detection of as little as 0.0_417 g. of Ce_2O_3. Benzidine acetate will also detect small amounts of Ce^{+4} due to the intense blue color developed.[5, 6] The spectroscope is, of course, an important tool in the detection of all rare earths, but misinterpretation of spectra has led many investigators to wrong conclusions.

9. Determination. — *Gravimetrically*, the rare earths may be separated as the oxalates or fluorides, converted to the oxides, and weighed as such. Further quantitative separations have not been worked out.[7] Cerium may be determined volumetrically, after oxidation to Ce^{+4}, by titration with a suitable reducing agent, the endpoint being determined electrometrically.[8]

[1] Pagel and Brinton, *J. Am. Ch. Soc.*, **51**, 42–56 (1929).

[2] Allison, *J. Am. Ch. Soc.*, **52**, 3796 (1930); *Phys. Rev.*, **30**, 66 (1927).

[3] A general discussion of the procedure is given by Mellor, V, p. 543 *et seq.*

[4] Noyes and Bray, p. 190, 209.

[5] Feigl, *Ch. Ztg.*, **44**, 689–90 (1920).

[6] For additional analytical data, see: Bur. Mines, Bull. 212, "Analytical Methods for Certain Metals, Including Cerium. . . . ," (1923).

[7] Hillebrand and Lundell, p. 437.

[8] See especially, Willard and Young, *J. Am. Ch. Soc.*, **50**, 1322–38 (1928); Furman, *Ibid.*, p. 755; Someya, *Z. anorg. allgem. Ch.*, **168**, 56 (1927). One of the best of the earlier methods is that of von Knorre, *Ber.*, **33**, 1924 (1900).

10. Oxidation and Reduction. — Ce^{+3} in acid solution is readily oxidized to Ce^{+4} by PbO_2, $S_2O_8^{--}$ and other strong oxidizing agents. Ce^{+4} is readily reduced by common reducing agents such as HI, H_2S, H_2SO_3, H_2O_2, HNO_2, Fe^{++}, $C_2O_4^{--}$ etc.[1] Ceric sulfate in H_2SO_4 solution is a strong oxidizing agent, capable of wide application.[2]

§157. Columbium.[3] (*Columbia*, i.e., the United States.) Cb = 93.3. Atomic No. 41. Valence 3 and 5. Discovered by Hatchett in 1801.

Tantalum. (Gr. *Tantalus.*) Ta = 181.4. Atomic No. 73. Valence (3), 5. Discovered by Ekeberg in 1802.

1. Physical Properties. —

	Columbium	Tantalum
Density	12.7	16.6
Melting point	1950°	*ca.* 3000°
Boiling point	>3300°	>4100°

Columbium and tantalum are like platinum in appearance, when polished; they are somewhat darker and bluer when unpolished. Pure tantalum is more ductile and malleable than columbium. Both metals can be rendered quite hard by cold working.[4] Tantalum was used between 1903 and 1911 as a filament in electric light bulbs but was displaced by tungsten. Before the advent of " all electric " radios, the interesting valve effect of tantalum caused it to be employed in rectifiers for charging storage batteries from an alternating current supply. Today the chief demand probably comes from manufacturers of radio tubes. In addition, some of the metal is used in jewelry, for chemical apparatus, e.g., high grade weights, dishes, electrodes, etc. The hindrance to extensive use of tantalum is that it cannot be heated much above 350° without absorbing gases and deteriorating. Commercial uses for columbium have not yet been found.

2. Occurrence. — Columbium and tantalum are usually found together.[5] Some of the more important ores are: columbite, $Fe(CbO_3)_2$, 83% Cb_2O_5; tantalite, $Fe(TaO_3)_2$, 86% Ta_2O_5; pyrochlore, a titanium, thorium, columbium mineral containing about 50% Cb_2O_5; samarskite, a more complex iron, calcium, uranium, rare earth, columbium, tantalum mineral, about 48% Cb_2O_5 and 20% Ta_2O_5, etc. These minerals are fairly widely distributed, but not in large deposits. The chief sources at present are western Australia and the Black Hills of South Dakota. Small amounts have also been found in South Africa, Canada, North Carolina, Scandinavia, Malaya[6] and elsewhere.[7] During 1928 production in the United States amounted to about 35,000 lbs. of ore, valued at slightly over $26,000. Metallic tantalum, 99.5% pure, is quoted at around 15¢ per gram.

3. Preparation. — The methods employed for the commercial preparation of metallic tantalum (and columbium) are trade secrets. The extraction of the oxides may be accomplished as follows:

The finely ground ore is fused with $K_2S_2O_7$. While still hot the melt is poured into water. After digestion for some time to dissolve the impurities, the supernatant liquid is removed and the precipitate treated with $(NH_4)_2S_x$ to extract any Sn or W. The residue from this operation contains Ta_2O_5 and Cb_2O_5. They may be subjected to fur-

[1] Benrath and Ruland, *Z. anorg. allgem. Ch.*, **114**, 267–77 (1920).

[2] Willard and Young, *loc. cit.;* Furman, *J. Am. Ch. Soc.*, **50**, 755–64 (1928).

[3] Often called Niobium.

[4] Cf. Heinrich and Petzold, *Ch. Fabrik*, **1928**, 689–91, *C.A.* **23**, 1015.

[5] Hillebrand and Lundell, p. 463, say that probably all natural columbates contain tantalum and that all tantalates contain columbium.

[6] This deposit may prove extensive.

[7] Cf. Bur. Mines, I. C. 6328, p. 9–10 (**1930**).

ther purification if desired. In order to separate Ta_2O_5 from Cb_2O_5, the oxides are dissolved in HF, the concentration of the solution carefully adjusted and Ta precipitated as K_2TaF_7, by addition of the right amount of KF. With proper control of conditions, four or five fractionations will yield a fairly complete separation.[1]

4. Oxides and Hydroxides. — While lower oxides have been reported, those of major importance are Cb_2O_5 and Ta_2O_5. Each is obtained as a white, infusible powder upon ignition of the metal, a lower oxide or the sulfide. The hydrated oxide is obtained as a gelatinous precipitate upon treating the solution of a columbate or a tantalate with H_2SO_4. Possibly the product is $HCbO_3 \cdot nH_2O$ or $HTaO_3 \cdot nH_2O$; perhaps the ortho-acid is obtained. In any case, ignition produces the pentoxide. The oxides are stable, slightly acidic, tasteless and odorless. When heated to a dull red, they glow and become crystalline.

5. Solubilities. — *a.* Metallic tantalum and columbium are not attacked by HCl, HNO_3 or aqua regia, hot or cold, dilute or concentrated. There is no reaction with hot, dilute H_2SO_4, but boiling, concentrated H_2SO_4 slowly dissolves them. The metals are soluble in HF and readily attacked by a mixture of HF and HNO_3.

b. The oxides, Cb_2O_5 and Ta_2O_5, are very stable. When pure and ignited at a high temperature, they are insoluble in all acids but HF, not attacked by Cl_2, HCl, CCl_4, Br_2, or HBr; dissolved by fusion with $K_2S_2O_7$, KOH, or Na_2CO_3, and borax. Before drastic ignition they may be completely volatilized in a current of HCl. Columbium pentoxide is converted to the chloride by CCl_4 at 220°; Ta_2O_5 is unaffected. Alkali hydroxides or carbonates do not dissolve Cb_2O_5 or Ta_2O_5. Tantalates of the composition $K_7[Ta(TaO_4)_4] \cdot 12H_2O$[2] are important because they form the only series of soluble tantalum salts known. Other alkali tantalates and tantalates of other metals are insoluble in H_2O. Solutions of columbates or tantalates, upon boiling, readily hydrolyze. The gelatinous precipitate obtained is said to be a hydrated oxide. The hydrate of Ta, prepared by precipitation from a cold, dilute solution, upon addition of dilute H_2SO_4, is soluble in the hot, concentrated acid and reprecipitates when cold and diluted. Hydrated Cb_2O_5 does not precipitate under these conditions.[3] Tantalic acid, when precipitated hot, is almost insoluble, and when precipitated cold is only slightly soluble in H_2O_2 (distinction from columbic and titanic acids).[4]

6. Reactions.[5] — Alkali columbates and tantalates are formed by fusion of the oxides. The soluble compounds are readily hydrolyzed upon boiling. Ammonium hydroxide, added to the solution of a columbate or tantalate, precipitates the hydrated oxide (hydroxide?). Hydrogen peroxide forms a stable per-acid, i.e., $HTaO_4 \cdot nH_2O$.[6] Potassium ferrocyanide produces, with columbates, a pale yellow precipitate; with tantalates, only a yellow color. The latter does not appear in the presence of oxalic, arsenic, tartaric, or citric acids. Potassium thiocyanate gives a bright yellow color with solutions of columbates (distinction from Ta and Ti). Zinc and concentrated HCl produce a blue to brown color in columbate solutions, even in the presence of fluorides (distinction from Ta). Titanium in large amount interferes due to the formation of a green color. A hydrofluoric acid solution of tantalum, when treated with KF, gives a crystalline precipitate of K_2TaF_7. Since the Cb salt is more soluble it is obtained upon concentration of the solution. A light brown precipitate forms when tannic acid is added to a tantalate; a red precipitate when added to a columbate.

7. Ignition. — A sodium meta-phosphate bead containing tantalum is colorless. If columbium be present, a blue bead is obtained in the reducing flame. The bead turns red if moistened with $FeSO_4$ and again heated.

8. Detection. — The separation of Cb and Ta from each other and especially from titanium is very difficult.[7] Reactions that are excellent when used with the individual

[1] Evans, II, p. 297; B. Mines, I. C. 6328, p. 12 (**1930**).

[2] The formula is uncertain.

[3] Weiss and Landecker, *Z. anorg. allgem. Ch.*, **64**, 86 (1909).

[4] Hahn and Gille, *Z. anorg. allgem. Ch.*, **112**, 283 (1920).

[5] Cf. Spitzin and Kaschtanoff, *Z. anorg. allgem. Ch.*, **182**, 207–27 (1929), *C.A.* **23**, 5425.

[6] Hillebrand and Lundell, p. 466, state that H_2O_2 does not give a color with Cb as commonly recorded in the literature.

[7] Cf. Noyes and Bray, p. 77; Hillebrand and Lundell, p. 464.

metals prove to be very unsatisfactory when applied to a mixture. According to Noyes and Bray,[1] the best method available for removal of Ti is to boil the precipitated hydroxides of Cb, Ta, Ti and Zr with a dilute solution of sodium salicylate and salicylic acid, whereupon all of the Ti is dissolved and the other three metals are left in the residue.[2] This latter is washed with HF, HNO_3 and H_2SO_4, and then fused with K_2CO_3. A cold water extraction removes Cb and Ta as $K_8Cb_6O_{19}$ and $K_8Ta_6O_{19}$. Boiling the solution with an acid (H_2SO_3) promotes hydrolysis. The precipitate of hydrated oxides of Cb_2O_5 and Ta_2O_5 may be dissolved in HF and the tantalum removed as K_2TaF_7 (see 3, above). Columbium can be detected in a portion of the oxide mixture by boiling with concentrated HCl and Zn, whereupon a blue color is obtained.

Another method for the separation of Cb from Ta depends upon " differential hydrolytic dissociation " of oxalotantalic and oxalocolumbic acids in presence of tannin in slightly acid ($H_2C_2O_4$) solution.[3] The tantalum precipitate is light brown in color; if contaminated with Cb it is red. Titanium, if present, also gives a red color and otherwise interferes.[4]

9. Determination. — Tantalum and columbium may be precipitated as the hydrated oxides, ignited to Ta_2O_5 and Cb_2O_5, respectively, and weighed as such.[5] *Volumetrically*, columbium can be determined by reduction to Cb^{+3} in a Jones reductor, and titration with standardized $KMnO_4$.

§158. Gallium[6] (L. *Gallia* = France). Ga = 69.72. Atomic No. 31. Valence (2), 3. Discovered by Boisbaudran in 1875.

The density of solid gallium is 5.904,[7] of the liquid, 6.095.[7] The melting point is 30.8°, the boiling point, 1700°. Gallium is a tough metal, soft enough to be cut with a knife. The color of a freshly exposed surface is like that of Hg°. Superficial oxidation, however, soon changes the appearance to a bluish gray. The metal is stable in air; upon heating, it does not burn below 500°. While Ga-Al alloys have been prepared, no commercial use for them has been found. Because of the wide temperature range at which Ga is liquid, it has been suggested as a substitute for Hg° in thermometers.[8]

Gallium is found in zinc blende, in iron ores (especially magnetite and pyrites), and in bauxite and china clay. Probably one of the richest sources known is the Bensberg black blende, which contains over 0.01% Ga. Another important source is the English ore used to make Middlesburgh pig iron.[9] It carries about 0.003% Ga. The chief American deposit is the zinc blende of Oklahoma. There the quantity is very small as is indicated by a report that the distillation of 12,000 lbs. of spelter left a residue containing only a few grams of gallium.[10]

[1] Cf. Noyes and Bray, p. 77; Hillebrand and Lundell, p. 464.
[2] Cf. Muller, *J. Am. Ch. Soc.*, **33**, 1506 (1911).
[3] Powell and Schoeller, *Analyst*, **50**, 485–98 (1925).
[4] Schoeller and Powell, *Ibid.*, **53**, 264 (1928); cf. Schoeller and Waterhouse, *Ibid.*, p. 515–20.
[5] See especially Hillebrand and Lundell, Chapt. 38.
[6] Browning, "Index to the Literature of Gallium, 1874–1903," Smithsonian Misc. Coll. 46, No. 1543, (**1904**). Fricke and Meyring, *Z. anorg. allgem. Ch.*, **176**, 325–48 (1928), *C.A.* **23**, 1073.
[7] Richards, *J. Am. Ch. Soc.*, **43**, 274 (1921).
[8] Boyer, *Ind. Eng. Ch.*, **17**, 1252–3 (1925).
[9] Hartley and Ramage, *J. Ch. Soc.*, **71**, 533 (1897).
[10] Hillebrand and Scherrer, *Ind. Eng. Ch.*, **8**, 225 (1916).

The preparation[1] of gallium involves the usual difficulties encountered when attempting to separate traces of one element from large amounts of another. Starting with an ore, the finely ground sample is digested with aqua regia. After removal of any residue and expulsion of the excess acid, the solution is treated with an excess of Zn°. The precipitated metals are filtered off and the filtrate is boiled for some time with more zinc. This produces a precipitate containing a basic gallium salt, zinc, aluminum, iron, etc. Further concentration of the Ga may be effected by dissolving the residue in HCl and fractionally precipitating with Na_2CO_3. Gallium is concentrated in the first portions. Fractional electrolysis of a slightly acid solution of the sulfates of Ga, In and Zn removes the Zn entirely and the Ga is obtained almost free from indium. The recovery of gallium from zinc flue dust is effected by solution of the dust in an excess of HCl, addition of $KClO_3$ and distillation to remove the germanium. The gallium is removed from the residue as indicated above. The preparation of metallic gallium is probably best effected by electrolysis of an alkaline gallate solution.

Metallic gallium is only slightly affected by water at room temperature, but action is vigorous at the boiling point. It dissolves in dilute HCl or NaOH with liberation of hydrogen. Cold, dilute HNO_3 has little effect. Aqua regia is a good solvent. Reaction with Cl_2 and Br_2 is vigorous at room temperatures, but I_2 requires the addition of heat.

Gallium oxide, Ga_2O_3, is obtained upon ignition of $Ga(OH)_3$ or $Ga(NO_3)_3$. It is white, infusible at a red heat, and almost insoluble in acids and alkalis. Gallium hydroxide, $Ga(OH)_3$ (?), white, gelatinous, is obtained when a solution of Ga^{+3} is treated with NH_4OH (tartrates interfere). The product is soluble in excess of the reagent or $(NH_4)_2CO_3$, but separates again upon boiling the solution. $Ga(OH)_3$ is readily soluble in the fixed alkali hydroxides, with the formation of a gallate, $MGaO_2$ (?). While at least one salt of Ga^{++} has been reported ($GaCl_2$), the more stable ion is Ga^{+3}, colorless. The sulfate, nitrate and chloride are all soluble in water, but hydrolyze readily on boiling, with the separation of a basic salt. Gallic chloride is deliquescent and volatile (addition of H_2SO_4 completely prevents volatilization).

Small amounts of Ga^{+3}, when boiled with ammonium acetate, are completely precipitated as $Ga(OH)_3$; sodium or barium carbonate effects the same result. Potassium ferrocyanide precipitates, from a 4 N HCl solution of Ga^{+3}, white, $Ga_4\,[Fe(CN)_6]_3$. This is a characteristic reaction and will detect 0.1 mg. of gallium. Gallic ion is not precipitated by H_2S, but in a slightly acid or an ammoniacal solution containing Ag, Zn, Mn, or AsO_3^{-3}, Ga_2S_3 completely separates, along with the other sulfides. Ga^{+3}, in neutral or slightly acid solution, gives a white precipitate when treated with HSO_3^-. Indium and large amounts of Zn interfere.

Gallium is separated from (1) Pb, Cu, Hg and As by H_2S in acid solution; (2) Fe, Ti, Tl, U, In and the rare earths by taking advantage of the greater solubility of $Ga(OH)_3$ in NaOH; (3) Co, Ni and Zn by precipitation of $Ga(OH)_3$ with NH_4OH in the presence of NH_4Cl. In the ordinary course of analysis, therefore, Ga^{+3} is precipitated in Group III, and, after the removal of Fe, remains to be separated from Al, Be, Cr and V. The last two are oxidized and the others reprecipitated with NH_4OH. After dissolving the hydroxides in concentrated HCl, the Ga^{+3} is removed as $Ga_4\,[Fe(CN)_6]_3$.[2] Another method involves the separation of Ga^{+3} and Fe^{+3} from other Group III ions by extraction from a 6 N HCl solution with ether. The Fe^{+3} is reduced to Fe^{++} by means of Hg° and the Ga^{+3} removed by again extracting as indicated above.[3] While Ga may be detected by means of $Fe(CN)_6^{-4}$, probably the best procedure is to examine the spark spectrum for the two bright lines in the violet (417.1mμ and 403.1mμ). In this way, 0.003 mg. of Ga can readily be detected.

[1] Cf. James and Fogg, *J. Am. Ch. Soc.*, **51**, 1459–60 (1929).
Boyer, Brit. Pat. 250,950, Aug. 12, 1925.
Richards and Boyce, *J. Am. Ch. Soc.*, **41**, 133 (1919).
Fogg and James, *Ibid.*, **41**, 947 (1919).
Dennis and Bridgeman, *Ibid.*, **40**, 1531–61 (1918).
Hillebrand and Scherrer, *Ind. Eng. Ch.*, **8**, 225 (1916).
Uhler and Browning, *Am. J. Sci.*, [4] **42**, 389–98 (1916).

[2] Browning and Porter, *Am. J. Sci.*, [4] **44**, 221 (1917).

[3] Noyes and Bray, p. 160.

Gravimetrically, gallium is determined by precipitation as $Ga(OH)_3$ with NH_4OH. The excess reagent is removed by boiling. The precipitate, after washing, is ignited to Ga_2O_3 and weighed.[1]

§159. Indium[2] (Characteristic spectral lines are indigo blue). In = 114.8. Atomic No. 49. Valence (1, 2), 3. Discovered by Reich and Richter in 1863.

The density of indium is 7.314;[3] its melting point, 155°;[4] and its boiling point 1450°.[4] The metal is silvery white, softer than lead, malleable, ductile and crystalline. It does not decompose water, even at the boiling point. At room temperatures indium is stable in dry air; on heating, it burns with a blue flame to In_2O_3. While less volatile than Zn or Cd, indium will sublime when heated in hydrogen or in a vacuum. A number of alloys have been prepared, but there is apparently no demand for them.

Indium occurs in zinc blende,[5] tungsten, tin and iron[6] ores. The principal source, however, is the flue dust from certain zinc smelters in which as much as 0.1% may be present. Extraction of the element from this material is effected by treating a sample with slightly less than enough HCl to completely dissolve all of the metal. Upon standing for some time, a spongy deposit separates that is composed of Pb, Cu, Cd, Fe, In, etc. It is dissolved in HNO_3 and evaporated with H_2SO_4 to remove any Pb. The filtrate is heated to boiling and then made slightly alkaline with NH_4OH, whereupon $Fe(OH)_3$ and $In(OH)_3$ precipitate. After filtration and washing with NH_4NO_3, the residue is dissolved in the minimum amount of HCl. The resulting solution is neutralized with NH_4OH and, after addition of an excess of $NaHSO_3$, boiled 15–20 minutes to precipitate the white basic sulfite, $In_2(SO_3)_3 \cdot In_2(OH)_6 \cdot 5H_2O$. This may be dissolved in H_2SO_4 and the indium reprecipitated as $In(OH)_3$ by means of NH_4OH.[7] Repetition of the last separation several times yields a product that, when ignited to In_2O_3, will contain not over 0.5% of impurities. Metallic indium is readily obtained by electrolyzing a sulfuric acid (25%) solution containing 20% of the oxide and 25% sodium citrate. A platinum anode, indium or iron cathode, and a current density of 2 amp./sq.dm. will yield a thick, compact deposit of the metal.[8]

Indium forms three oxides, InO, In_2O_3 and In_3O_4. The suboxide, InO, is obtained by carefully heating In_2O_3 in hydrogen at 300°. The product is black, pyrophoric and slowly soluble in acids. Light yellow In_2O_3, is obtained when In is burned in air or when the carbonate, nitrate or sulfate is ignited below 850°. This oxide is readily soluble in acids, especially hot, dilute H_2SO_4. In_3O_4 is formed by heating In_2O_3 above 850°.

Indium dissolves in mineral acids and $H_2C_2O_4$, but not in $HC_2H_3O_2$ or the fixed alkalis. It unites directly with the halogens and sulfur. The most stable salts are those of In^{+3}.

[1] Cf. Ato, *Sci. Papers Inst. Phys. Ch. Research (Tokyo)*, **12**, 225–9 (1930), *C.A.* **24**, 2689; Moser and Brukl, *Monatsh.*, **50**, 181–92 (1928), *C.A.* **23**, 577; *Monatsh.*, **51**, 325–33 (1929), *C.A.* **23**, 3185; Brukl, *Monatsh.*, **52**, 253–9 (1929), *C.A.* **23**, 5433; Kirshmann, *et al.*, *J. Am. Ch. Soc.*, **50**, 1632–6 (1928).

[2] Cf. Browning, "Index to the Literature of Indium, 1863–1903." Smithsonian Misc. Coll., No. 1571, **1905**. A summary of Winkler's work is to be found in *Ann. ch. phys.*, [4] **13**, 490 (1868).

[3] Richards and Sameshima, *J. Am. Ch. Soc.*, **42**, 49 (1920).

[4] Mott, *Trans. Am. Electroch. Soc.*, **34**, 287 (1918).

[5] Hartley and Ramage, *Proc. Roy. Soc. (London)*, **68**, 99 (1901); *J. Ch. Soc.*, **71**, 533 (1897).

[6] Siderite.

[7] Winkler, *loc. cit.*; Bayer, *J. Ch. Soc.*, **24**, 664 (1871); Hillebrand and Lundell, p. 379; Mellor, V, p. 388–9.

[8] Westbrook, *Trans. Am. Electroch. Soc.*, **57**, 289 (1930); cf. Mathers, *J. Am. Ch. Soc.*, **29**, 485 (1907); Dennis and Geer, *Ibid.*, **26**, 437 (1904).

The nitrate, sulfate, alums and halides are soluble in H_2O. They hydrolyze readily, forming slightly soluble basic salts. The sulfate is very hygroscopic; the chloride deliquescent.

If In^{+3} is treated with an alkali hydroxide, a gelatinous white precipitate of $In(OH)_3$ is obtained. The precipitate is insoluble in NH_4OH. It is peptized by the fixed alkali hydroxides and reprecipitated on boiling. It has only slight acidic properties, the meta-indate ion, InO_2^-, being formed.[1] Sodium, ammonium or barium carbonate precipitates In^{+3} as $In_2(CO_3)_3$, insoluble in the fixed alkali carbonates, soluble in $(NH_4)_2CO_3$ but reprecipitated if the solution is boiled. Oxalic acid and alkali oxalates precipitate In^{+3} as $In_2(C_2O_4)_3{\cdot}6H_2O$,[2] insoluble in NH_4OH. A solution of In^{+3} boiled with sodium acetate, forms a basic indic acetate only slightly soluble in water. Alkali cyanides form a white precipitate of $In(CN)_3$, soluble in excess of the reagent. If the resulting solution is diluted and boiled, indic hydroxide separates. Potassium ferrocyanide gives a white precipitate with In^{+3}, the ferricyanide or thiocyanate has no visible effect. The ferrocyanide, $In_4\,[Fe(CN)_6]_3$, is more soluble in HCl than the corresponding gallium salt. Disodium phosphate gives a voluminous white precipitate with In^{+3}.

Hydrosulfic acid, added to a neutral or acetic acid solution of In^{+3}, precipitates yellow In_2S_3, soluble in mineral acids and the fixed alkali sulfides, partially soluble in hot $(NH_4)_2S_x$, with the formation of a white residue. If the solution is allowed to cool, a voluminous white precipitate is obtained. Hydrosulfic acid added to an alkaline solution, or $(NH_4)_2S$ added to a neutral solution of indium, forms a white precipitate (possibly $In(HS)_3$). Sodium thiosulfate, added to a neutral solution of In^{+3}, gives a precipitate of indium sulfite; in an acid solution the product is the sulfide. The reaction is incomplete in either case.

If potassium chromate is added to a neutral solution of In^{+3} a yellow precipitate separates; addition of a dichromate produces no apparent action. Ammonium molybdate precipitates In^{+3} as $In_2(MoO_4)_3{\cdot}2H_2O$,[3] ammonium metavanadate also forms a precipitate.[4, 5]

A volatile indium salt colors the Bunsen burner flame blue violet. Two characteristic brilliant lines appear in the spectrum[6] — 451.15mμ and 410.2mμ. Heated in the reducing flame on charcoal with fusion mixture, indium compounds give a metallic bead and a yellow incrustation of the oxide. If $In(OH)_3$ is ignited at 800°–850°, In_2O_3 is formed;[7] above 850°, In_3O_4 is obtained; and at 1000°, volatilization takes place.

Probably one of the most direct tests for indium in an ore involves the following steps: (1) Digestion of the sample with aqua regia; (2) removal of any insoluble residue and excess acid; (3) addition of sodium acetate; (4) saturation with hydrogen sulfide; (5) extraction of the precipitate with hydrochloric acid; (6) examination of the HCl solution spectroscopically for the two lines.[8]

The separation of indium from zinc may be accomplished by dissolving the metal in acid. The indium, together with any iron present, is precipitated as the hydroxide by addition of NH_4OH. After filtration and washing, the residue is dissolved in acetic acid and the In^{+3} removed as In_2S_3 by saturating the solution with H_2S.[9]

In the usual qualitative procedure, indium is precipitated in Group III and left in the

[1] Renz, *Ber.*, **34**, 2763 (1901).

[2] Huysse, *Z. anal. Ch.*, **39**, 9 (1900).

[3] Renz, *Ber.*, **34**, 2763 (1901).

[4] *Ibid.*

[5] For additional data concerning indium compounds, see: Thiel and Koelsch, *Z. anorg. allgem. Ch.*, **66**, 288–321 (1910), *C.A.* **4**, 2613; Mathers and Schluederberg, *J. Am. Ch. Soc.*, **30**, 211–15 (1908), *C.A.* **2**, 962.

[6] Uhler and Tauch, *Astrophys. J.*, **55**, 291 (1922).

[7] Hillebrand and Lundell, p. 381.

[8] Dennis and Bridgeman, *J. Am. Ch. Soc.*, **40**, 1534 (1918), state that 0.0013 mg. of indium can be detected by examination of the spark spectrum of HCl solutions, and that large amounts of gallium do not interfere.

[9] Mathers, *J. Am. Ch. Soc.*, **30**, 209 (1908), removes traces of iron by precipitation with nitroso-β-naphthol from an acetic acid solution.

residue after treatment with NaOH and H_2O_2. If iron and gallium have been previously removed by extraction, this residue will consist of indium, titanium, zirconium and the rare earths.[1] The first three may be removed with HF and the indium precipitated from the nearly neutral[2] solution by addition of H_2S. If the sulfide precipitate is not yellow it should be dissolved in HNO_3, the In^{+3} separated as $In(OH)_3$ by means of NH_4OH and again converted to In_2S_3.[3]

Indium may be determined by precipitation as $In(OH)_3$, ignition to In_2O_3 at 800° and weighing. Chlorides should be absent because of the volatility of indium chloride when ignited.[4]

§169. Thorium (*Thor* = Scandinavian god). Th = 232.12. Atomic No. 90. Valence 4. Discovered by Berzelius in 1828.

1. Physical Properties. — Density, 11.3–11.7, depending upon previous treatment;[5] melting point, 1845°;[6] boiling point >3000°. Metallic thorium is said to exist in two forms, one crystalline and the other a gray, glistening powder. The metal as ordinarily encountered is dark gray and contains some oxide. Thorium is stable in air at room temperature, on gentle heating it ignites and burns with a brilliant flame to ThO_2. At 450° thorium burns in Cl, Br, I or S; at 650° it combines with either H or N. Thorium is more electropositive than Mg; it alloys readily with various metals, e.g., Al, Cu, Ni, Zn. When mixed with 1% of CeO_2 and strongly heated, ThO_2 emits a brilliant light which property gives rise to its most important use, i.e., for gas mantles.[7] A small amount of Th is used for making electric light filaments.

2. Occurrence. — Although small deposits of thorite (*ca.* 60% ThO_2 present as the silicate) and thorianite (*ca.* 80% ThO_2) have been exploited, by far the largest amount of thorium has been obtained from monazite sand, which carries 3%–9% ThO_2 as the phosphate. The chief sources of monazite sand are (1) Brazil, which produced about 2070 tons in 1928, (2) Travancore, India, furnishing slightly over 100 tons in the same year, and (3) the Carolinas in the United States, which supplied only a very small amount. The Brazilian sand as prepared for exportation contained 5%–7% ThO_2 and was valued at $8–$10 per unit.[8]

3. Preparation. — Monazite sand, as mined, is concentrated on shaking tables and by use of electromagnetic separators. The concentrate is pulverized and digested with strong H_2SO_4 for several hours. The resulting mixture is slowly poured into cold H_2O and the residue of silica, rutile, zircon, etc., removed by filtration. If necessary, the filtrate may be treated with H_2S to eliminate Group II metals. After their removal, careful neutralization of the solution will precipitate thorium phosphate. This product is dissolved in HCl and upon addition of oxalic acid, $Th(C_2O_4)_2 \cdot 6H_2O$ is precipitated. After washing, the precipitate may be ignited, dissolved in HCl and converted to the

[1] Also Group IV elements. Noyes and Bray, p. 190, *et. seq.*

[2] NH_4OH is used.

[3] Cf. Wada and Ato, *Rep. Inst. Phys. Ch. Research* (*Tokyo*), **1**, 57 (1922), who have studied the analytical reactions of indium.

[4] Hillebrand and Lundell, p. 381–2. Cf. Moser and Siegmann, *Monatsh.*, **55**, 14–24 (1930), *C.A.* **24**, 2081.

[5] Rentschler and Marden, *Phys. Rev.*, **25**, 589 (1925). Cf. Friend, V, 282.

[6] Landolt-Bornstein, V. Cf. Rentschler and Marden, *loc. cit.*

[7] The "Welsbach" mantle, in addition to 1% CeO_2, is said to contain a small amount of Be and of Mg to give strength to the skeleton. For a description of the fabrication of mantles, see: Hopkins, p. 187; Johnstone, "Rare Earth Industry," p. 15, or Levy, "Rare Earths," p. 265.

[8] A unit is 1% per ton, i.e., a sand containing 6% ThO_2 would be worth $48–$60 per ton. For data used in this calculation, see: Mineral Ind. **1929**.

nitrate, which is the usual commercial salt.[1] In order to obtain metallic thorium, probably the best method is to heat ThO_2 with metallic calcium and $CaCl_2$ in a bomb. Among other methods that have been suggested are (1) electrolysis of the fused chloride which gives a distinctly impure product; (2) action of Na° on $ThCl_4$; (3) action of Na° on the double alkali fluoride or chloride; (4) the thermite process.

4. Oxides and Hydroxide. — The principal oxide of thorium is the dioxide, ThO_2. It occurs in nature as thorianite and may be prepared by igniting the hydroxide, oxalate or any thorium salt of a volatile oxygen acid. When pure it is white and appears to possess no acidic properties. Another oxide, Th_2O_7, has been mentioned but is of negligible importance. Thorium hydroxide, $Th(OH)_4$, is obtained by treating Th^{+4} with a base. The precipitate is gelatinous and white.

5. Solubilities. — Metallic thorium dissolves readily in aqua regia. It is also soluble in HCl, less readily in H_2SO_4 and HF, while in HNO_3 it soon becomes passive. It is not attacked by the alkali hydroxides. Thorium oxide, ThO_2, is insoluble in acids except hot, concentrated H_2SO_4. It is not affected by fusion with the alkalis. Thorium hydroxide, when freshly precipitated, is readily soluble in acids but after drying is more resistant. It is soluble in the alkali carbonates. Thorium chloride and nitrate are soluble in water, the anhydrous sulfate is soluble in ice water, but on heating it separates as a hydrate. If the solution is allowed to stand without boiling, a series of hydrates will separate, their composition depending upon conditions. This behavior of $Th(SO_4)_2$ is important in that it may be used for the quantitative separation of Th^{+4} from ions of the other earths. Among the slightly soluble salts are $ThOCO_3{\cdot}8H_2O$, $Th(C_2O_4)_2{\cdot}6H_2O$, $ThFe(CN)_6$, $K_2ThF_6{\cdot}4H_2O$, $Th_3(PO_4)_4{\cdot}4H_2O$ and $K_4Th(SO_4)_4{\cdot}H_2O$. Thorium oxalate is soluble in solutions of the alkali oxalates and reprecipitated on addition of a mineral acid.

6. Reactions. — Thorium forms only one series of salts, namely those of the tetravalent ion, Th^{+4}, the reactions of which resemble those of Ce^{+4}. Th^{+4} forms an insoluble hydroxide with NaOH or NH_4OH. The precipitate is insoluble in excess of the reagent and is not formed in the presence of organic oxy-acids (separation from yttrium). Alkali carbonates precipitate Th^{+4} as a basic carbonate,[2] readily soluble in an excess of the concentrated reagent, difficultly soluble in a dilute solution of the reagent. Barium carbonate completely precipitates Th^{+4} from a cold solution. The precipitate is said to be $Th(OH)_4$.[3] Oxalic acid precipitates Th^{+4} from a mineral acid solution as thorium oxalate, $Th(C_2O_4)_2{\cdot}6H_2O$ (distinction from Al and Be), white, practically insoluble in an excess of the reagent and only slightly soluble in dilute mineral acids, but readily soluble in a mixture of ammonium acetate and acetic acid (distinction from Ce and Yt earths), soluble in a hot concentrated oxalate solution with formation of complex ions, e.g., $Th(C_2O_4)_4^{-4}$. Boiled with a solution of sodium acetate, Th^{+4} forms a precipitate of a basic acetate. Treated with $K_4Fe(CN)_6$, Th^{+4} gives a white precipitate of $ThFe(CN)_6$ in neutral or slightly acid solutions. The test is very delicate. Hydrogen peroxide precipitates Th^{+4} as a peroxyhydrate, especially on warming the neutral or slightly acid solution. The precipitate is soluble in an excess of H_2SO_4.[4] The addition of sodium phosphate to a solution containing Th^{+4} produces a gelatinous precipitate of $Th_3(PO_4)_4{\cdot}4H_2O$.[5] The insolubility of thorium pyrophosphate in dilute acid solution is the basis for an excellent quantitative method for the separation of Th^{+4} from cerium and determination of the Th^{+4}.[6]

Sulfides in acid solution do not affect Th^{+4}, in alkaline solution the hydroxide, $Th(OH)_4$, is precipitated. If $Na_2S_2O_3$ is added to a solution of Th^{+4} and the whole boiled, a precipitate of $Th(OH)_4$ and sulfur is obtained (distinction from Ce). If H_2SO_4 is mixed with

[1] Details are not available. Cf. Carney and Campbell, *J. Am. Ch. Soc.*, **36**, 1134 (1914), for another practicable method.

[2] See Chauvenet, *Compt. rend.*, **153**, 66–8 (1911), *C.A.* **5**, 3021, for a discussion of the carbonates of Th.

[3] U. S. Bur. Mines Bull. 212, p. 25.

[4] Cf. Schwarz and Giese, *Z. anorg. allgem. Ch.*, **176**, 209–32 (1928), *C.A.* **23**, 786.

[5] The composition of the precipitate depends upon conditions and which salt of phosphoric acid is added. Cf. d'Ans and Dawihl, *Z. anorg. allgem. Ch.*, **178**, 252-6 (1929), *C.A.* **23**, 2115.

[6] Carney and Campbell, *J. Am. Ch. Soc.*, **36**, 1134–43 (1914).

a solution of Th^{+4} and heated, a basic sulfate will precipitate which will dissolve on cooling. A saturated solution of K_2SO_4 forms, with Th^{+4}, an insoluble double salt that is not affected by an excess of the reagent but is dissolved by hot water (separation from the Yt earths). The corresponding sodium and ammonium double salts are soluble in water and in an alkali sulfate solution (distinction from the cerite earths).[1]

The addition of HF or a fluoride to a solution of Th^{+4} produces a bulky white precipitate of ThF_4, insoluble in excess of the reagent (separation from Al, Be, Zr, Ti). Thorium forms a number of insoluble double fluorides of the type xKF·$y$$ThF_4$. If ThO_2 is suspended in NaOH and the system saturated with Cl_2, no dissolving takes place (distinction from many other earths but not cerium oxide). If potassium hydronitride is boiled with Th^{+4} a precipitate of $Th(OH)_4$ is obtained. It has been stated[2] that this is possibly one of the most distinctive reactions for Th^{+4}.[3] Sodium azide, NaN_3, gives a similar reaction. The test is distinctive if Ce is in the tervalent state.

7. Ignition. — Thorium chloride sublimes at a low red heat. The oxalate and other salts of volatile oxy-acids give ThO_2 upon ignition.

8. Detection. — Thorium forms a soluble chloride, no sulfide in presence of water, and a hydroxide insoluble in a slightly alkaline solution. It is therefore, a member of Group III and may be precipitated with the other metals of that group.[4] The precipitate may be dissolved in HCl and the Ce and Th separated from other members of Group III by precipitation as oxalates.[5] Since this step does not give a separation from the other rare earths, the oxalate precipitate may be ignited, the oxide residue dissolved and treated with KIO_3 in concentrated HNO_3, after reduction of Ce^{+4} to Ce^{+3}, or the Th^{+4} and Ce^{+4} may be precipitated together and the precipitate warmed with HNO_3 and H_2O_2, adding a little KIO_3. This reduces the Ce^{+4} to Ce^{+3} and leaves the thorium iodate as a residue.[6] Another mode of procedure for the separation of Th^{+4} from the phosphates of tervalent rare earth metals is to precipitate thorium as the pyrophosphate from a sulfate or chloride solution approximately 0.3 *N*. Confirmatory tests involve the following: (1) precipitation of the peroxyhydrate by means of H_2O_2;[7] (2) pyrogallol aldehyde gives a yellow color and precipitate with Th^{+4};[8] (3) Th^{+4} in a neutral solution of the rare earths when treated with sebacic acid gives a precipitate of thorium sebacate;[9] (4) since thorium has radioactive properties it may be detected with the electroscope as are radium ores.[10]

9. Determination. — The quantitative determination of thorium in a solution free from Zr and the rare earths merely involves precipitation of $Th(OH)_4$ or $Th(C_2O_4)_2 \cdot 6H_2O$, ignition to the oxide and weighing as such. Usually preliminary separations from Zr, Ti, Sc, other Group III elements, the rare earths, etc., are necessary. These may be effected by the pyrophosphate[11] or iodate[12] methods.[13] *Volumetrically,* Th may be determined using ammonium molybdate as the standard solution and diphenylcarbazide as an external indicator.[14] Some experience is required to detect the endpoint.

[1] Cf. Rüdisüle, VI, p. 970 *et. seq.*

[2] Browning, p. 73.

[3] Cf. Dennis and Kortright, *Am. Ch. J.*, **16**, 79 (1894).

[4] Cf. §156, p. 371.

[5] Schoeller and Powell, "The Analysis of Minerals and Ores of the Rarer Elements," Charles Griffin & Company, London, **1919**.

[6] Meyer, *Z. anorg. allgem. Ch.*, **71**, 65–9 (1911).

[7] Wyrouboff and Verneuil, *Bull. soc. ch.*, [3] **19**, 219 (1898).

[8] Zr produces a similar product upon boiling or after addition of H_2O_2. Kaserer, *Ch. Ztg.*, **42**, 170 (1918), *C.A.* **12**, 2174.

[9] Smith and James, *J. Am. Ch. Soc.*, **34**, 281–4 (1912).

[10] Helmick, *J. Am. Ch. Soc.*, **43**, 2003 (1921).

[11] Carney and Campbell, *loc. cit.*

[12] Meyer, *loc. cit.*

[13] For details and other methods see: Hillebrand and Lundell, p. 418, *et. seq.*; Moore, *et al.*, U. S. Bur. Mines Bull. 212; Rüdisüle, VI, 2, 978.

[14] Metzger and Zons, *Ind. Eng. Ch.*, **4**, 493 (1912).

§170. Titanium (*Titans* = giants of Greek mythology). Ti = 47.90. Atomic No. 22. Valence (2), 3 and 4. Discovered by Gregor in 1791.

1. Physical Properties. — Density, 4.49;[1] melting point, 1795° ± 15°;[2] boiling point > 3000°. Amorphous titanium is a dark gray powder. The fused metal resembles polished steel. When cold it is very brittle, but at a red heat may be forged and drawn into wire.[3] The ductility is low, however. Carbon-free Ti is hard enough to scratch glass; rubbed against steel it gives off bright sparks. It is almost as good a conductor of electricity as Al. In general properties, Ti resembles Ce, Th, Zr and Hf. At 610° it burns in oxygen and at 800° unites directly with nitrogen. It combines with the halogens to form the corresponding tetravalent salt. At lower temperatures the metal is fairly stable. There is at present practically no demand for metallic titanium. The alloy, ferro-titanium, has been used extensively in the iron and steel industry as a "scavenger"; copper-titanium (10% Ti) and manganese-titanium (30% Ti) have been used for the same purpose in preparing brass and bronze castings. While other alloys, as with Sn, Al, Cr, Co, Mo and W, have been prepared, they appear to have but slight commercial use. Probably the greatest tonnage of Ti is employed at present in the paint industry, where TiO_2 is used as a white pigment[4] due to its remarkable opacity or covering power and its stability. A small amount is also used in making printing inks and in the glass and ceramic industries.

2. Occurrence. — Titanium is present in practically all rocks. Comprising 0.62% of the earth's crust,[5] it is ninth in abundance among the elements, outranking many of the so-called "common" elements, as Pb, Cu, Zn, etc. There are commercially two important ores, rutile and ilmenite. The former is titanium dioxide, TiO_2, and is found in Virginia, Canada, Norway, Australia, Madagascar, etc. Until a few years ago, practically all of the titanium used was supplied by the Kragerö mines in Norway. At present the Virginia deposits, believed to be the most extensive in the world, are perhaps a more important source. Rutile is marketed as a concentrate containing 94%–96% TiO_2. The wholesale price is (1931) 12¢–15¢ a pound. Ilmenite is generally considered to be $FeTiO_3$, containing, when pure, about 53% titanium, calculated as TiO_2. Although ilmenite is a usual component of monazite sand and as such is found in Brazil, Florida, etc., at present the most important source is Travancore, India. Should the demand arise another mineral, magnetite, can be profitably utilized as a source of titanium.

3. Preparation. — In Virginia the titanium ore is crushed to the size of coarse sand, the titanium minerals concentrated on shaking tables, dried and the ilmenite removed by means of a magnetic separator. The rutile remaining is about 95% TiO_2, while the ilmenite runs slightly over 50% TiO_2.

Metallic titanium may be prepared from TiO_2 by conversion to the tetrachloride, $TiCl_4$, which in the vapor phase reacts with sodium hydride to give Ti°.[6] The chloride may also be reduced with Na° in a high pressure bomb.[7] The product is said to be less pure than that obtained by the first method. Van Arkel and de Boer[8] believe that a more satisfactory procedure is to reduce the tetra-iodide, TiI_4, at 650° and deposit the metal on a tungsten filament.

4. Oxides and Hydroxides. — Titanium is said to form at least four oxides, TiO, Ti_2O_3, TiO_2 and TiO_3. Titanium monoxide, TiO, has been prepared by reduction of TiO_2 with

[1] Patterson, *Phys. Rev.*, [2] **26**, 56 (1925).

[2] Burgess and Waltenberg, *Proc. Wash. Acad. Sci.*, **3**, 371 (1913); *Z. anorg. allgem. Ch.*, **82**, 371 (1913).

[3] Anderson, *J. Franklin Inst.*, **184**, 467 (1917).

[4] See U. S. Pat. 1,106,409; 1,106,410; 1,171,521; also Thornton, "Titanium," A. C. S. Monograph No. 33, pp. 66–68.

[5] U. S. Geol. Survey, Prof. Paper 127.

[6] Billy, *Ann. ch.*, **16**, 5–54 (1921), *C.A.* **16**, 1051.

[7] Hunter, *J. Am. Ch. Soc.*, **32**, 330 (1910).

[8] van Arkel and de Boer, *Z. anorg. allgem. Ch.*, **148**, 345–50 (1925).

carbon or magnesium at a high temperature. It is basic, unstable and of no practical importance (possibly because its properties are unknown). Titanium sesquioxide, Ti_2O_3, is obtained as black lustrous crystals, upon heating TiO_2 in hydrogen. The corresponding hydroxide, $Ti(OH)_3$, forms a gelatinous, dark colored precipitate when a solution of Ti^{+3} is treated with an alkali. This compound is very unstable. Titanium dioxide, TiO_2, is the common form of Ti found in nature. When pure it is white (cf. 7), but as ordinarily encountered, it is distinctly brown due to impurities. The hydroxide, $Ti(OH)_4$, is amphoteric; as a base it forms titanic salts, Ti^{+4}, and as a weak acid it acts chiefly as a metatitanate, TiO_3^{--}, which hydrolyzes readily to $TiO_2 \cdot xH_2O$. Some investigators believe that orthotitanates do not exist.

5. Solubilities. — Metallic titanium is readily soluble in HF, but in the absence of H_2SO_4 much Ti may be lost due to the volatility of TiF_4. In hot dilute HCl Ti° dissolves to form Ti^{+3} if oxidizing agents are excluded. Dilute HNO_3 attacks Ti slowly in the cold, forming titanic acid; if the reagent is hot and concentrated, metatitanic acid, H_2TiO_3, is formed which is difficultly soluble. Ti° is soluble in aqua regia, but a coating of titanic acid forms that soon stops the reaction. Cold, dilute H_2SO_4 readily dissolves Ti° to form Ti^{+3}; the hot, concentrated acid gives Ti^{+4} and SO_2. Oxidizing agents in general readily attack Ti°. Ferro-alloys, low in Si and Ti, are soluble in hot H_2SO_4 or HNO_3, but the reaction becomes slower the higher the Ti content. If HNO_3 is used it must generally be removed before further steps are taken in analysis. Ti_2O_3 is insoluble in HCl and in HNO_3, soluble in H_2SO_4. Titanium dioxide is insoluble in H_2O and practically insoluble in the ordinary dilute acids; concentrated HCl, HNO_3 and aqua regia have only a slight effect. Hot concentrated H_2SO_4 slowly converts TiO_2 to the sulfate, $Ti(SO_4)_2$, which is soluble in H_2O if sufficient acid is present to prevent hydrolysis. Alkali hydroxides have only a slight solvent effect on TiO_2 (cf. 7), while a saturated solution of Na_2CO_3 is without action. Titanic hydroxide, if prepared by precipitation from a cold solution, is readily soluble in dilute acids and alkali carbonates, especially $(NH_4)_2CO_3$. Titanous salts are in general readily soluble in H_2O, forming a wine-red to violet solution, depending upon the acidity. Among the titanic salts the ferrocyanide and phosphate are insoluble. Practically all of those soluble require the presence of some acid to prevent hydrolysis. A good solvent for titanium compounds in general is a mixture of HF and H_2SO_4 containing a small amount of HNO_3.[1]

6. Reactions.[2] — Salts of Ti^{+4} hydrolyze readily when put in H_2O. The precipitate formed in the cold may be $Ti(OH)_4$. If, however, separation takes place from a boiling solution, the precipitate is metatitanic acid, $TiO(OH)_2$ (or H_2TiO_3). When a solution of Ti^{+4} is treated with NaOH, NH_4OH or $BaCO_3$, in the absence of a tartrate,[3] a white gelatinous precipitate is obtained, its composition depending on the temperature as indicated above. The ortho- compound is readily soluble in acids, slightly soluble in NaOH; the meta- compound is insoluble. Soluble oxalates precipitate Ti^{+4} as white titanium oxalate. Boiled with sodium acetate Ti^{+4} forms metatitanic acid. Potassium ferrocyanide forms with Ti^{+4} a brown precipitate; the ferricyanide yields a yellow product.

A solution of Ti^{+4} when treated with H_2O_2, gives a yellow to red color,[4] depending on the concentration of Ti^{+4}. This reaction forms a very delicate test[5] for titanium in the absence of fluorides, phosphates and large amounts of alkali salts, which tend to bleach the color. Ferric ion tends to interfere due to its color; Cr^{+3} gives blue H_3CrO_8; Mo gives a yellow, vanadium a red-brown, color. The composition of the product obtained with Ti^{+4} is still an open question. It is said to be peroxytitanic acid and the formulas H_2TiO_4 and H_4TiO_5 have been suggested.[6]

[1] U. S. Bur. Mines Bull. 212.

[2] For the reactions of Ti^{++} and Ti^{+3} see: Pfordten, *Ann.*, **234**, 257 (1886); **237**, 201 (1887). A bibliography on hexavalent Ti is given by Faber, *Z. anal. Ch.*, **46**, 277 (1907).

[3] Many organic compounds, pyrophosphates, etc., interfere with precipitation of titanic hydroxide.

[4] Schönn, *Z. anal. Ch.*, **9**, 41 (1870).

[5] As little as 0.3 mg. in 100 cc. of solution gives a distinct color. Wells, *J. Am. Ch. Soc.*, **33**, 504 (1911).

[6] Cf. Schwarz and Sexauer, *Ber.*, **60B**, 500 (1927), whose results indicate $TiO_2 \cdot O \cdot 2H_2O$; Billy, *Compt. rend.*, **172**, 1411 (1921); Faber, *Z. anal. Ch.*, **46**, 277–91 (1907).

When Ti^{+4} is treated with an alkali phosphate, e.g., Na_2HPO_4, a white precipitate of a basic phosphate, approximately $Ti(OH)PO_4$, is obtained even in a fairly strongly acid solution (separation from Al). Tartrates do not interfere, but H_2O_2 in a cold solution prevents precipitation (distinction from Zr). When $(NH_4)_2S$ is added to a solution of Ti^{+4} a precipitate of titanium hydroxide is obtained, ortho- if cold, meta- if hot. Boiling Ti^{+4} with $Na_2S_2O_3$ quantitatively precipitates the Ti^{+4} as the hydroxide (distinction from tervalent ions of the rare earth metals but similar to Al, Zr, Th, Sc and Ce^{+4}). The same result is obtained with H_2SO_3. Sodium hyposulfite, $Na_2S_2O_4$ (often called hydrosulfite), reacts with Ti^{+4} in dilute acid to give a red to violet solution of Ti^{+3}.[1] Unless protected by an inert atmosphere, the color quickly disappears.

Many organic compounds form colored products with Ti^{+4}, especially in concentrated H_2SO_4.[2] Thymol gives a yellow to deep red color.[3] The test must be performed in a solution of not less than 80% H_2SO_4 and in the absence of tungsten. The reaction is said to be 25 times more delicate than the peroxide test.[4] Dihydroxy-maleic acid gives a brilliant orange color with Ti^{+4}.[5] Vanadium does not interfere seriously, since it gives a blue color. Molybdenum and uranium give a red to brown color readily destroyed by warming with acids. Tungsten gives a brown color quickly changing to blue. Ferric and fluoride ions interfere, while Th, Ce and Zr have no effect. In a Ti^{+4} solution containing one part of Ti in a thousand, tannic acid gives a brownish precipitate soon turning orange.[6] The color is bleached by acids, restored by alkalis. Iron interferes. Cupferron forms a flocculent, canary yellow precipitate with Ti^{+4}. Precipitation is effected even in a strongly acid solution. In general, organic compounds do not interfere. Fe^{+3}, Cu^{++}, Zr, Th, Sn^{+4}, V, U, Cb and Ta also form precipitates, while Si, W, Ce, Ag, Pb, Hg and Bi are partially precipitated. As with Al^{+3}, phenylhydrazine precipitates Ti^{+4} as the hydroxide.

7. Ignition. — Titanium dioxide when heated turns yellow. It becomes white again when cooled. Mixed with microcosmic salt, TiO_2 forms a yellow bead when hot, colorless when cold. Prolonged heating in the reducing flame produces a violet color due to the formation of tervalent Ti. The same result may be obtained more rapidly by fusing a mixture of microcosmic salt, TiO_2 and Sn on a piece of charcoal. A borax bead is only faintly colored when fused with TiO_2.[7] Fusion with NaOH and Na_2CO_3 is a good method for converting insoluble Ti compounds to an easily dissolved form. The Ti becomes Na_2TiO_3 which, on leaching the melt with H_2O, is left in the residue but is readily soluble in acids. A better fusion mixture is NaOH and Na_2O_2 in the ratio 1 : 4. Best of all in most cases is potassium pyrosulfate ($K_2S_2O_7$).

8. Detection. — Titanium is found in Group III if sufficient acid is present during the separation of previous groups to prevent its precipitation by hydrolysis. Its detection in Group III is readily effected by the peroxide test (see 6, above) in the absence of Cr, V, Mo, W, PO_4^{-3}, etc. If any of these elements are present, the Group III precipitate should be fused with Na_2CO_3 and the cold melt leached with H_2O. After filtration, the residue, dissolved in H_2SO_4, is tested for Ti by means of H_2O_2.[8] To detect Ti in a mineral or ore, a finely powdered sample is fused with Na_2CO_3 and NaOH, the melt extracted with H_2O, the residue dissolved in H_2SO_4, and the solution tested as indicated above.

9. Determination. — While titanium may be determined *gravimetrically* by precipitation as the hydroxide, ignition to TiO_2 and weighing as such, this procedure is seldom

[1] Fresenius, *Z. anal. Ch.*, **24**, 410 (1885).

[2] Hall and Smith, *Proc. Am. Phil. Soc.*, **44**, 196 (1905).

[3] Lenher and Crawford, *J. Am. Ch. Soc.*, **35**, 138 (1913). The reagent should be dissolved in glacial acetic acid, then diluted with 10% alcohol to a concentration of 1% thymol.

[4] Hauser and Lewite, *Ber.*, **45**, 2480 (1912), have shown that all phenols, especially polyhydric phenols with adjacent hydroxyl groups, give a similar reaction with Ti^{+4}.

[5] Fenton, *J. Ch. Soc.*, **93**, 1064 (1908). Cf. Piccard, *Ber.*, **42**, 4341 (1909); Fenton, *Ibid.*, **43**, 267 (1910).

[6] Das-Gupta, *J. Ind. Ch. Soc.*, **6**, 855–63 (1929), *C.A.* **24**, 1820.

[7] Lutz, *Z. anal. Ch.*, **47**, 21 (1908).

[8] Browning, *et al.*, *Am. J. Sci.*, [4] **42**, 106–8 (1916); Noyes and Bray, *J. Am. Ch. Soc.*, **29**, 137 (1907).

employed. Large amounts of the element may be determined *volumetrically* by reducing Ti^{+4} to Ti^{+3} with zinc. The solution thus obtained is allowed to react with ferric sulfate in the absence of air and the Fe^{++} produced is titrated with standardized $KMnO_4$. Small amounts of Ti may be determined colorimetrically by addition of H_2O_2 to a solution of $Ti(SO_4)_2$ and comparison of the yellow color with that formed in a solution of known Ti content.[1]

10. Oxidation and Reduction. — Metallic titanium, dissolved in cold, dilute HCl or H_2SO_4 in the absence of air, forms Ti^{+3}, deep red to violet. Hot, concentrated H_2SO_4 or HNO_3 gives Ti^{+4}. Tervalent titanium is a very powerful reducing agent. It readily changes Cu^{++} to Cu°,[2] Fe^{+3} to Fe^{++}, etc., being itself oxidized to Ti^{+4}. Its usefulness is greatly limited, however, because it must be protected from atmospheric oxygen which quickly produces Ti^{+4}. Quadrivalent titanium is reduced to Ti^{+3} by Zn°, Sn°, Na amalgam, Mg°, Al° in acid solution.[3] Reduction to Ti° is effected only with very powerful reducing agents as Na° and NaH at higher temperatures.

§171. Uranium (Planet *Uranus*). U = 238.14. Atomic No. 92. Valence (2), (3), 4, (5), 6, (8?). Discovered by Klaproth[4] in 1789.

1. Physical Properties. — Density, 18.7;[5] melting point, <1850°.[6] The boiling point has not been determined. Metallic uranium resembles nickel in appearance. It is ductile, malleable and capable of taking a high polish. A brightly polished surface is stable in dry air but tarnishes in a few days when exposed to the atmosphere. In the finely divided state U° takes fire on exposure to air while larger pieces will burn briskly when heated to 170°. Uranium slowly decomposes water at room temperature, the action being fairly rapid at the boiling point. The metal is highly electropositive. It has no important commercial applications, a small amount being used in the ceramic industry to make yellow glazes[7] and in the dyeing industry as a mordant. Some uranium has been used as a substitute for tungsten in steel, but there is little demand for such an alloy, possibly because of the cost.

2. Occurrence. — The principal ores of uranium are pitchblende,[8] carnotite and autunite. Pitchblende contains 75%–90% U_3O_8. It is green to black in color and has a pitchy luster. The oldest known and probably most celebrated deposit is at Joachimsthal (Jachymov), in Czechoslovakia, where the mines have been worked since early in the sixteenth century.[9] Other deposits are found in Cornwall, England and in Gilpin County, Colorado. Carnotite is a double vanadate of potassium and uranium, $K_2(UO_2)_2(VO_4)_2{\cdot}8H_2O$, and contains 62%–65% uranium oxide. Probably the largest deposit in the world is in southwestern Colorado and eastern Utah. Until the much richer radium ore was found in the Belgian Congo, the Colorado district furnished practically all of the ore for the radium industry.[10] Autunite, a calcium uranium phosphate, $(CaUO_2)_2PO_4{\cdot}8H_2O$, found principally in Portugal and Australia is of minor importance as

[1] For details and other methods, see: Thornton, "Titanium," A. C. S. Monograph No. 33; Hillebrand and Lundell, Chapt. 37; U. S. Bur. Mines Bull. 212.

[2] Knecht, *Ber.*, **41**, 498 (1908).

[3] Ruff and Neumann, *Z. anorg. allgem. Ch.*, **128**, 81 (1923).

[4] Klaproth's "metal" was actually the oxide, as shown by Péligot in 1842.

[5] I. C. T.

[6] B. Stds. Cir. 35; cf. Guertler and Pirani, *Z. Metallkunde*, **11**, 1–7 (1919), *C.A.* **14**, 664.

[7] As little as 0.006% of $Na_2U_2O_7{\cdot}6H_2O$ gives a good yellow color. Other colors are obtained by varying the amount of the salt.

[8] Often called uraninite.

[9] They are now used chiefly as sources of radioactive water for the famous Spas.

[10] Recently a very rich deposit of pitchblende has been reported in the Great Bear Lake region of upper Canada.

a source of uranium. From a commercial standpoint, uranyl nitrate, $UO_2(NO_3)_2 \cdot 6H_2O$, is the most important compound; next in order is the acetate, $UO_2(C_2H_3O_2)_2 \cdot 2H_2O$. In 1929 there were 272,913 lbs. of the oxide and various salts imported into the United States. The total valuation was almost $345,000.

3. Preparation. — Since radium is the most valuable component of all uranium ores, usually the primary objective is the winning of that element. Uranium is therefore generally a by-product, and methods for its recovery are modified accordingly. Of the various procedures available for its direct isolation, the following are apparently most satisfactory. (1) The mineral is digested with HNO_3, then evaporated to dryness and the residue extracted with H_2O. This aqueous solution is concentrated to produce crystals of the uranium nitrate which may be purified by recrystallization. (2) The ore is roasted to remove sulfur and arsenic, then heated in a reverberatory furnace with Na_2CO_3 or Na_2SO_4. The melt is extracted with dilute H_2SO_4, the filtrate treated with excess Na_2CO_3 to precipitate impurities. The filtrate, containing sodium uranyl carbonate, is neutralized, whereupon sodium diuranate, $Na_2U_2O_7 \cdot 6H_2O$, yellow, separates, is filtered off and dried. (3) Carnotite is fused with $K_2S_2O_7$ and the melt extracted with H_2O. The solution thus obtained is evaporated to precipitate the double sulfates of K, U and V. Reduction with Zn° and H_2SO_4, followed by precipitation of the V with $(NH_4)_2CO_3$, leaves a filtrate from which ammonium diuranate may be obtained by boiling off the excess reagent. If the product is ignited it becomes U_3O_8, which in turn may be heated with carbon (coke) in an electric furnace to give metallic uranium 96%–98% pure. Another method for securing the metal is to reduce UCl_4 with Na°[1] or Ca°.[2] The product is purer than that from the first procedure. A third method suggested is electrolysis of the fused salt. It is apparently less satisfactory than the others.

4. Oxides[3] and Hydroxides. — The following oxides have been reported: UO_2, U_2O_5, UO_3, U_3O_8 and UO_4. Among them only the first and third have been well established, while the fourth, U_3O_8, is believed to be a mixture, $UO_2 \cdot 2UO_3$. Uranium dioxide, UO_2, brown to black, is obtained when U° is burned at 150°–170° or when U_3O_8 is heated in hydrogen at 625–50°. Uranium trioxide, UO_3, brick red,[4] is formed when uranic acid, ammonium diuranate, or ammonium uranyl carbonate is heated to not over 300°. This oxide, like WO_3 and MoO_3, is amphoteric, but its acid properties are much less pronounced. Two hydrates of UO_3 are known: the yellow monohydrate, $UO_3 \cdot H_2O$, and the dihydrate, $UO_3 \cdot 2H_2O$ (or $H_2UO_4 \cdot H_2O$). The former may act as uranic acid, H_2UO_4, or as uranyl hydroxide, $UO_2(OH)_2$. Uranic acid is dibasic. It forms salts of the type R_2UO_4 also $R_2O \cdot xUO_3$, where x may range from 2 to 6, the most important class being the diuranates, $R_2O \cdot 2UO_3$ or $R_2U_2O_7$. Salts of this type are usually precipitated when metallic oxides, hydroxides or carbonates are added to solutions of uranyl salts. The green oxide, U_3O_8 (i.e., $UO_2 \cdot 2UO_3$), is obtained by heating ammonium diuranate or any oxide of uranium to 700° in air.

5. Solubilities. — *a.* Metallic uranium is soluble in HCl or HNO_3, slowly soluble in cold, dilute H_2SO_4 to form U^{+4} salts. The caustic alkalis have no apparent action.

b. Uranium dioxide is soluble in HNO_3 and aqua regia, difficultly soluble in HCl, HBr and H_2SO_4. The oxide U_3O_8 is insoluble in H_2O, readily soluble in HNO_3[5] but dissolves with difficulty in HCl (distinction from V_2O_5). It also is readily soluble in a mixture of glacial acetic acid and HNO_3 (20 : 1) (distinction from ignited V_2O_5 and Fe_2O_3 which are practically insoluble).

c. In general, uranates are insoluble in H_2O, soluble in acids. Most uranyl salts are soluble in H_2O. Those insoluble are dissolved by HCl. Uranyl ferrocyanide is soluble in NaOH, HCl or $(NH_4)_2CO_3$. The resulting solution is yellow. Uranyl sulfide, UO_2S, is insoluble in H_2O, readily soluble in $(NH_4)_2CO_3$ (distinction from Zn, Mn, Fe, etc.). Uranium tetrafluoride, UF_4, is insoluble in H_2O; the hexafluoride, UF_6, is readily soluble. Uranyl phosphate is insoluble in H_2O.

[1] Moore, *J. Am. Electroch. Soc.*, **43**, 317 (1923); Hunter and Jones, *Ibid.*, **44**, 27 (1923).

[2] Jander, *Z. anorg. allgem. Ch.*, **138**, 321 (1924); James, *et al.*, *Ind. Eng. Ch.*, **18**, 114–6 (1926).

[3] Cf. Jolibois and Bossuet, *Compt. rend.*, **174**, 386–8 (1922), *C.A.* **16**, 1367; Lebeau, *Compt. rend.*, **174**, 388–9 (1922).

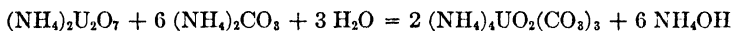
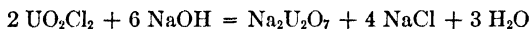
[4] Two forms have been described, one orange yellow, the other red.

[5] Hopkins says that the ignited oxide is difficultly soluble in mineral acids.

6. Reactions. — The salts of uranium may be divided chiefly into two classes: (1) the uranous,[1] U^{+4}, green in color and strong reducing agents; (2) the uranyl,[2] UO_2^{++}, yellow in color with a strong greenish fluorescence. They are more important than the tetravalent compounds. The ion UO_2^{++} is distinctly basic. Its salts of strong acids are not appreciably hydrolyzed. Among the salts in which uranium is in the anion, the diuranates, $R_2U_2O_7$, are most important.[3]

a. Sodium or ammonium hydroxide gives with U^{+4} a pale green precipitate of uranous hydroxide, $U(OH)_4$ (or $UO_2 \cdot 2H_2O$), insoluble in excess reagent and rapidly oxidizing on exposure to air with a change in color to brown. No precipitate is obtained in the presence of tartaric acid or excess CO_3^{--}. Alkali carbonates or bicarbonates give a pale green precipitate with U^{+4}. The precipitate is soluble in $NaHCO_3$ or $(NH_4)_2CO_3$ and reprecipitated from the former on boiling, but not from the latter unless the excess is removed. Barium carbonate completely precipitates U^{+4} even in the cold. Sodium or ammonium hydroxide, free from CO_3^{--}, quantitatively precipitates[4] UO_2^{++} as the diuranate, $R_2U_2O_7$, yellow, insoluble in excess reagent, readily soluble in $(NH_4)_2CO_3$.

$$2\,UO_2Cl_2 + 6\,NaOH = Na_2U_2O_7 + 4\,NaCl + 3\,H_2O$$

$$(NH_4)_2U_2O_7 + 6\,(NH_4)_2CO_3 + 3\,H_2O = 2\,(NH_4)_4UO_2(CO_3)_3 + 6\,NH_4OH$$

No precipitate is formed in the presence of a tartrate or peroxide. In the latter case, a deep yellow to red solution of a peruranate is formed. The alkali carbonates give with UO_2^{++} a yellow precipitate of, e.g., $Na_4UO_2(CO_3)_3$, readily soluble in excess reagent. If Na_2CO_3, solid or a concentrated solution, and H_2O_2 are added to a solution of UO_2^{++} a red color appears. Barium carbonate completely precipitates UO_2^{++}, probably as $Ba_2UO_2(CO_3)_3$ (distinction from Ni, Co, Mn and Zn).[5]

b. Uranyl salts are slowly reduced by soluble oxalates. Potassium ferrocyanide gives with U^{+4} a yellow-green precipitate, gradually oxidizing to red brown; with UO_2^{++}, a deep red-brown precipitate of $(UO_2)_2Fe(CN)_6$[6] is obtained.[7] This product may be distinguished from $Cu_2Fe(CN)_6$ by treatment with NaOH, HCl, or $(NH_4)_2CO_3$, all of which dissolve the precipitate with formation of a yellow solution. Potassium ferricyanide reacts with U^{+4} to form $Fe(CN)_6^{-4}$ and UO_2^{++} which combine to give the red precipitate described above.

c. Uranyl salts give with H_2O_2 (30%) a pale yellow precipitate of $UO_4 \cdot xH_2O$,[8] soluble in excess reagent. If Na_2CO_3 or $(NH_4)_2CO_3$ is present a deep yellow to red color appears. This is a delicate test for U (Cr, Ti and V interfere).

d. If Na_2HPO_4 is added to a solution containing UO_2^{++} a pale yellow precipitate of UO_2HPO_4 is obtained, soluble in mineral acids, insoluble in acetic acid or acetates. In the presence of ammonium salts $UO_2NH_4PO_4 \cdot xH_2O$ separates. Vanadium does not interfere, though Al, Be and Pb do.

e. In an acid solution, H_2S does not precipitate U^{+4} or UO_2^{++}. Ammonium sulfide forms with U^{+4}, in neutral solution, a pale green precipitate of US_2 (?), which rapidly darkens; with UO_2^{++} a dark brown precipitate of uranyl sulfide, UO_2S, is formed. This product is insoluble in excess of the reagent, but if the mixture is aerated, a red compound is obtained due to $(NH_4)_2S_2O_3$. Uranyl sulfide is insoluble in NH_4OH, readily soluble in $(NH_4)_2CO_3$ (distinction from Zn, Mn, Fe, etc.) and in acids. No precipitate is formed in the presence of a tartrate. Uranyl thiosulfate, $UO_2S_2O_3$, yellow, is precipitated when $Na_2S_2O_3$ is added to a solution of UO_2^{++}. A flocculent, yellow precipitate separates when $(NH_4)_2SO_3$ is the reagent. Apparently in contrast to other U^{+4} salts,

[1] Regarding uranous salts see: Zimmermann, *Ann.*, **216**, 10 (1883), *Z. anal. Ch.*, **23**, 66 (1884).

[2] Apparently only one salt of the type UX_6 has been prepared, i.e., UF_6.

[3] Cf. de Coninck, *Bull. acad. roy. Belg.*, **1908**, 992–5; **1909**, 173–5, *C.A.* **4**, 29–30, 1948.

[4] In the absence of V.

[5] Kohn, *Z. anorg. allgem. Ch.*, **50**, 315 (1906), discusses the similar action of $ZnCO_3$.

[6] Some investigators give $K_2UO_2Fe(CN)_6 \cdot 6H_2O$.

[7] Small amounts of UO_2^{++} give only a brown color.

[8] The amount of H_2O varies with the temperature. Rosenheim and Daehr, *Z. anorg. allgem. Ch.*, **181**, 177–82 (1929).

uranous sulfate, $U(SO_4)_2$, is fairly stable in air. Uranyl sulfate is probably not a simple salt because under various conditions $BaCl_2$ gives a precipitate of $BaSO_4$ only after long standing.[1]

f. Hydrofluoric acid and soluble fluorides form with U^{+4} a precipitate of UOF_2; with UO_2^{++} no precipitate is obtained.

7. Ignition. — Uranium compounds do not color a non-luminous flame. Beads of borax or sodium metaphosphate give a yellow color in the oxidizing, green in the reducing flame.[2] Uranium trioxide, UO_3, is formed when uranic acid, ammonium diuranate, or ammonium uranyl carbonate is heated to not over 300°. Heated to 700° all oxides and many of the salts form U_3O_8.

8. Detection. — Uranium normally appears in Group III, being precipitated as $(NH_4)_2U_2O_7$. Precipitation is usually incomplete, however, unless precautions are taken to use a reagent free from carbonate. Uranium may be separated from other ions of Groups III and IV by precipitating them with $(NH_4)_2S$ in the presence of $(NH_4)_2CO_3$. A separation from ions of Groups V and VI may be effected by precipitation of UO_2S with $(NH_4)_2S$ in the presence of NH_4Cl. The uranyl ion, UO_2^{++}, can be separated from Cr and V by use of an alkali phosphate,[3] and from U^{+4} by precipitation of the latter as the fluoride.

Uranium, as UO_2^{++}, may be detected[4] by treating a solution of $UO_2(NO_3)_2$ with an excess of Zn°, whereupon a yellow deposit of $UO_3 \cdot 2H_2O$ (?) forms on the residual Zn°. The test may be applied to the HNO_3 extract of an ore. Large amounts of Fe or V interfere, also HCl and H_2SO_4. Other metals likely to be present do not.[5]

Potassium ferrocyanide gives a red-brown precipitate with UO_2^{++} that may be distinguished from $Cu_2Fe(CN)_6$ by means of NaOH (cf. 6, *b*). A delicate test for uranium involves the addition of $TlNO_3$ to a solution containing UO_2^{++} and CO_3^{--}. A crystalline precipitate is obtained which is very insoluble in water.

Various "physical" tests have been suggested for uranium. Since uranium compounds are radioactive, the electroscope may be used for their detection (Th and other radioactive elements interfere). Uranic salts, exposed to violet light, give a beautiful fluorescence. Uranous salts are not affected.[6]

A number of organic reagents have been suggested for use in detecting uranium. Cupferron is interesting in that it gives a precipitate with U^{+4} but not with UO_2^{++}. Advantage is taken of this difference to separate UO_2^{++} from V, Fe, Ti and Zr in H_2SO_4 solution. After filtration the uranium can be reduced to U^{+4}, precipitated with more cupferron, and thus separated from Al, Cr, Mn, P, etc.[7] Aliphatic α-hydroxyl and ketonic acids, also aromatic hydroxycarboxylic acids and higher phenols (pyrogallol, hydrochinone, gallic acid, sodium salicylate, etc.), give characteristic colors with uranyl salts.[8] A 10% solution of ethylenediamine produces a bright yellow, crystalline precipitate with uranium salts, soluble in excess of the reagent. The reaction is about as delicate as the $K_4Fe(CN)_6$ test, but many other elements interfere.[9] Thiosinamine in alkaline solution gives a yellow precipitate with UO_2^{++}. Apparently no other heavy metal (except Cd) or alkaline earth gives a precipitate with this reagent.[10] Turmeric paper, dipped in a slightly acid solution of UO_2^{++}, turns brown. If the paper is next

[1] Giolitti *et al.*, *Gazz. ch. ital.*, **35**, II, 145–70 (1905); **36**, II, 443–50 (1906).

[2] For many details regarding the bead test, see Rüdisüle, V, 1148–50.

[3] Browning, *J. Am. Ch. Soc.*, **43**, 114 (1921).

[4] See 6 for reactions distinguishing U^{+4} from UO_2^{++}.

[5] Buell, *Ind. Eng. Ch.*, **14**, 593 (1922); Baur and Rebmann, *Helv. Ch. Acta*, **5**, 221 (1922).

[6] Aloy and Auber, *Bull. soc. ch.*, [4] **1**, 569–71 (1907), *C.A.* **1**, 2446; cf. Papish and Hoag, *Proc. Natl. Acad. Sci.*, **13**, 726–8 (1927).

[7] Auger, *Compt. rend.*, **170**, 995 (1920); Angeletti, *Gazz. ch. ital.*, **51**, I, 285 (1921); Martimi, *Anales asoc. quím. Argentina*, **16**, 117-24 (1928), *C.A.* **23**, 1841.

[8] Das-Gupta, *J. Indian Ch. Soc.*, **6**, 763–76 (1929), *C.A.* **24**, 1312; Müller, *Ch. Ztg.*, **43**, 739–40 (1920), *C.A.* **14**, 1945.

[9] Siemssen, *Ch. Ztg.*, **35**, 139, 742 (1911), *C.A.* **5**, 1886.

[10] Lemaire, *Repert. Pharm.*, **20**, 433 (1908).

treated with Na_2CO_3 it becomes very dark in color. Large amounts of mineral acid interfere with the test.

9. Determination. — Uranium may be separated from other elements by the methods indicated above (cf. 8). Possibly the most important separations are those based on the use of $(NH_4)_2CO_3$. The determination of uranium *gravimetrically* may be effected by (a) precipitation with carbonate-free ammonia as $(NH_4)_2U_2O_7$, ignition to and weighing as U_3O_8;[1] (b) precipitation by $(NH_4)_2HPO_4$ in the presence of $NH_4C_2H_3O_2$ as $UO_2NH_4PO_4$,[2] ignition to and weighing as $UO_2P_2O_7$; (c) precipitation as UO_2S followed by ignition and weighing as U_3O_8 (although complete precipitation is difficult to attain, the results tend to be somewhat high due to oxidation of sulfide to sulfate).[3] *Volumetrically*, UO_2^{++} may be reduced to U^{+4} by means of a Jones reductor and titrated with $KMnO_4$.

$$2\,KMnO_4 + 5\,U(SO_4)_2 + 2\,H_2O = 2\,KHSO_4 + 2\,MnSO_4 + H_2SO_4 + 5\,UO_2SO_4$$

Some investigators consistently obtained high results due to partial reduction to a lower stage. Others claim that the method is very satisfactory.[4] The determination of the endpoint electrometrically has also been advocated.[5] The titration of $UO_2(C_2H_3O_2)_2$ with standardized sodium phosphate, using $K_4Fe(CN)_6$ as an external indicator has also been suggested. Apparently considerable experience is necessary before reliable results can be obtained. *Electrolytically*, uranium can be quantitatively precipitated at the anode as the hydrated oxide, which may be ignited to U_3O_8 and weighed.[6] *Colorimetrically*, small amounts of uranium may be determined by means of the red color that develops when UO_2^{++} reacts with sodium salicylate.[7]

10. Oxidation and Reduction. — Solutions of Sn, Pt, Au, Cu, Hg and Ag are reduced to the metal by U°.[8] Uranous ion, U^{+4}, in acid solution is also a strong reducing agent. It will precipitate Ag or Au from solutions of their salts. The uranyl ion, UO_2^{++}, is readily reduced to U^{+4} by Zn°, Mg°, Cd°, Sn°, Pb°, Co°, Cu°, Fe° and Fe^{++}, slowly by $C_2O_4^{--}$. UO_2^{++} is not reduced by H_2S, SO_2 or $SnCl_2$.

§172. Vanadium (*Vanadin* = Scandinavian goddess). V = 50.96. Atomic No. 23. Valence 2 to 5. Discovered by A. M. del Rio in 1801; rediscovered in 1830 by Sefström.

1. Physical Properties. — Density, 5.82;[9] melting point, 1720° ± 20°;[10] boiling point, 3400° (calc.).[11] Vanadium is obtained as a grayish powder or silvery crystals, depending upon the purity. Exposure to air causes oxidation; on ignition, V_2O_5 is formed. Vanadium is harder than any other metal (approximately 7 on Mohs' scale). It can be cold rolled into wire. It is only feebly magnetic. The chief uses for vanadium are: (1) in alloy steels where it imparts hardness and toughness (the amount used is seldom over

[1] With care, this method, one of the oldest, will give good results. V and CO_3^{--} must be absent. Cf. Bur. Mines Bull. 212 (1923).

[2] This precipitate is not easily filtered.

[3] Cf. Schwarz, *Helv. Ch. Acta*, **3**, 330–46 (1920), *C.A.* **15**, 641; Pierlé, *Ind. Eng. Ch.*, **12**, 60–3 (1920).

[4] Cf. Hillebrand and Lundell, 370; Furman and Schoonover, *J. Am. Ch. Soc.*, **53**, 2561 (1931).

[5] Ewing and Eldridge, *J. Am. Ch. Soc.*, **44**, 1484 (1922); Gustavson and Knudson, *Ibid.*, p. 2756.

[6] Kern, *J. Am. Ch. Soc.*, **23**, 685–726 (1901).

[7] Müller, *Ch. Ztg.*, **43**, 739 (1919).

[8] Zimmermann, *loc. cit.*

[9] Prandtl and Manz, *Z. anorg. allgem. Ch.*, **79**, 209 (1913); Marden and Rich, *Ind. Eng. Ch.*, **19**, 786–8 (1927).

[10] B. Stds. Cir. 35.

[11] Mott, *Trans. Am. Electroch. Soc.*, **34**, 255 (1918).

1%); (2) as a catalyst in the manufacture of dyes, sulfuric acid, etc. Vanadium readily alloys with many metals, but little attention has been paid to these alloys.

2. Occurrence. — While vanadium occurs widely scattered in small amounts, the chief commercial source is Minas Ragra, Peru. This locality furnishes practically all of the ore used. The deposit there is patronite, a complex containing V_2S_5. In 1928 some 500 tons were shipped, but the year before, about 6,000 tons were exported. The ore contains 11%–12% of vanadium and is valued at around $100 per ton.

3. Preparation. — Practically all of the vanadium of commerce is sold in the form of ferrovanadium (30%–40% V) since 90% of the world's production is used in the iron and steel industry. (a) The sulfide ore is first roasted to remove sulfur. The product is fused with Na_2CO_3 and the sodium vanadate thus formed is leached out. Addition of concentrated H_2SO_4 to the solution gives a precipitate of V_2O_5. This concentrate is mixed with iron and by aluminothermite reduction converted to ferrovanadium. (b) The sulfide ore may be mixed with iron and fed into an electric furnace, where carbon reduces the V_2S_5, and the V thus liberated combines with molten iron to form the desired alloy.

4. Oxides and Hydroxides. — Vanadium forms four[1] oxides: VO, gray; V_2O_3, black; VO_2, dark blue; and V_2O_5, dark red to orange red. Hypovanadous oxide, VO (also written V_2O_2), is formed by passing the vapor of vanadium oxytrichloride ($VOCl_3$), mixed with H_2, over hot carbon. The gray product, contaminated with carbon, dissolves in dilute acids without the evolution of H_2, to form lavender hypovanadous acid, one of the most powerful reducers known. If the solution is made alkaline with a fixed alkali, brownish $V(OH)_2$ is obtained. Vanadium trioxide, V_2O_3, black, is obtained when the pentoxide is heated in hydrogen. This oxide is not easily soluble in either acids or alkalis. The properties of vanadous salts are similar to those of Fe^{+3}, Cr^{+3} and Al^{+3}, except that the V^{+3} is a stronger reducing agent than Cr^{+3}. Like Fe^{+3} the vanadous ion readily forms complex cyanides. Vanadous hydroxide, $V(OH)_3$, green, is obtained upon neutralizing the solution of a vanadous salt. Hypovanadic oxide, VO_2 (or vanadium tetroxide, V_2O_4), dark blue, is obtained by fusing the pentoxide with $H_2C_2O_4$ or by electrolysis of the molten pentoxide. The tetroxide is somewhat hygroscopic. The dihydrate, $V_2O_4{\cdot}2H_2O$, exists in two forms, one stable and green, the other unstable and red. This oxide has both acidic and basic properties. Vanadium pentoxide, V_2O_5, dark red to orange,[2] is the most important oxide. It may be obtained by roasting the sulfide ore, patronite (see above).[3] It melts between 650° and 700°. It is poisonous. Moistened, it turns blue litmus red. This oxide forms vanadic salts, e.g., V^{+5}; and vanadates. These do not fit nicely into the subdivisions, ortho- VO^{-3}, pyro- $V_2O_7^{-4}$, and meta- VO_3^-, but may be referred to the general formula $H_{n+2}V_nO_{3n+1}$.[4] Further complications arise in connection with the formation of vanadic salts, in that some of the oxygen tends to remain as part of the positive ion; e.g., $VOCl_3$, VO_2F, $V_2O_5{\cdot}2SO_3$. Heteropolyacids are also readily obtained.

5. Solubilities. — *a. Metal.* — Vanadium is not attacked by solutions of the alkalis. It is insoluble in HCl, slowly dissolves in HF, hot, concentrated H_2SO_4, HNO_3, or aqua regia.

b. Oxides and Hydroxides. — VO is insoluble in H_2O but dissolves in acids, with evolution of hydrogen, to form a lavender solution. V_2O_3 is attacked by HNO_3 and HF, but is apparently insoluble in the alkalis and other acids. The hydroxide, $V(OH)_3$, is basic and insoluble in the alkalis. VO_2 (or V_2O_4) is insoluble in H_2O; readily soluble in acids and alkalis. V_2O_5 (red) dissolves to the extent of 300–400 mg./l. in H_2O.[5] It is readily soluble in strong acids, forming salts that hydrolyze easily. Concentrated H_2SO_4 forms

[1] V_2O_7 has apparently not been isolated. The existence of V_2O is somewhat uncertain.

[2] V_2O_5 exists in 3 forms: yellow amorphous, red amorphous, and crystalline. The red is the one commonly encountered.

[3] Bleecker, *Met. Ch. Eng.*, 8, 667 (1910), says that V_2O_5 is most easily made by the hydro-electrolysis of a fused copper vanadate ingot, and that the product thus obtained may be 100% pure.

[4] See: Mellor, IX, p. 758.

[5] Bleecker, *Met. Ch. Eng.*, 8, 667 (1910).

a blood-red solution that turns blue on dilution.[1, 2] The best solvent appears to be either Na_2CO_3 or NaOH, with a small amount of peroxide. Depending on conditions in the alkaline medium, ortho-, meta-, or pyro-vanadates may be formed (see above), of which the meta-, e.g., $NaVO_3$, is the most stable.[3]

c. Salts. — Among the salts, VOCl and VOBr are slightly soluble in H_2O, readily soluble in HNO_3;[4] $V_2(SO_4)_3$ is insoluble in H_2O;[5] $VOBr_2$ dissolves in H_2O to give a blue solution. The alkali vanadates are soluble in H_2O;[6] NH_4VO_3 is least soluble, and quantitatively precipitated by NH_4Cl, in the presence of alcohol. Many of the heavy metal vanadates are insoluble in H_2O or $HC_2H_3O_2$, especially when a slight excess of the precipitant is present. There is a tendency for the precipitate to become colloidal. This is most pronounced with Fe, Cu, Zn and Al; least with Pb, Hg and Ca. The meta-salts are decomposed by mineral acids, with formation of vanadyl salts. If the solution is highly concentrated, V_2O_5 will precipitate.

6. Reactions. — $VOSO_4$ or $VOCl_2$, treated with an alkaline hydroxide or carbonate, gives a grayish precipitate of $VO_2 \cdot nH_2O$.

Metavanadates are the most stable. Solutions of alkali metavanadates are colorless; acidification causes a change in color to yellow or orange, due to the formation of polyvanadate. The best known series of these compounds is the 2 : 3 series, i.e., $2R_2O_5 \cdot 3V_2O_5$. All simple Na–V compounds are decomposed by mineral acids with formation of vanadyl salts. If the solution is concentrated, V_2O_5 precipitates.

Acid vanadate solutions yield a brown precipitate with alkalis, soluble in excess, to give a yellow color. Potassium ferrocyanide gives a green precipitate (composition not settled), insoluble in mineral acids.[7] Hydrogen peroxide oxidizes vanadates in cold, acid (15%–20% H_2SO_4)[8] solution, to deep red pervanadic acid, HVO_4, more stable than perchromic acid, but destroyed by excess H_2O_2.[9] This reaction readily reveals one part of vanadium in 5000 parts of solution. An acid solution of a vanadate gives no precipitate with H_2S.[10] Reduction to the tetravalent state takes place. Ammonium sulfide forms a thiovanadate, which colors the solution brown. Acidification causes incomplete precipitation of V_2S_5, which is soluble in alkalis, alkali carbonates and sulfides.[11] Vanadium halides are hygroscopic and tend to hydrolyze more readily, the higher the valence. If to a solution of a vanadate, neutral or alkaline, solid NH_4Cl be added, the vanadium is completely precipitated as NH_4VO_3, ammonium metavanadate, colorless, crystalline, insoluble in NH_4Cl solution. Upon ignition in air or oxygen, V_2O_5 is obtained. Neutral or slightly acid vanadate solutions form precipitates with the heavy metals.[12] $Pb(C_2H_3O_2)_2$ forms a basic lead vanadate, yellow, turning to white on standing. Precipitation under suitable conditions is quantitative. $Hg_2(NO_3)_2$ precipitates yellow mercurous vanadate, which upon ignition forms Hg and V_2O_5. Silver vanadate, yellow to orange, is obtained in a neutral solution (like Ag_3AsO_4). Ba^{++} forms a yellow precipitate of $Ba(VO_3)_2$ (distinction from PO_4^{-3} and AsO_4^{-3}), which becomes colorless on standing. Cupric ion may be used to distinguish pyro- from metavanadates. Cupric pyrovanadate is a yellow, crystalline precipitate, while the metavanadate is green.

[1] Cf. Sieverts and Müller, *Z. anorg. allgem. Ch.*, **173**, 313–23 (1928), *C.A.* **23**, 1583.

[2] Meyer and Aulich, *Ibid.*, **194**, 278–92 (1930), have considered the solubility of especially purified V_2O_5 in H_2SO_4.

[3] Fischer, *Trans. Am. Electroch. Soc.*, **30**, 190 (1916).

[4] Ruff and Lickfett, *Ber.*, **44**, 506 (1911).

[5] Stähler and Wirthwein, *Ber.*, **38**, 3980 (1905).

[6] $NaVO_3$, 21.1 g. in 100 g. H_2O at 25°; NH_4VO_3, 10 g./l. in the cold.

[7] This reaction has been suggested for the determination of V in steel by Evans and Clarke, *Analyst*, **53**, 475 (1928).

[8] Meyer, *Ch. Ztg.*, **53**, 366 (1929), *C.A.* **23**, 4640.

[9] Meyer and Pawletta, *Z. physik. Ch.*, **125**, 49 (1927). Cf. Idem., *Z. angew. Ch.*, **39**, 1284–6 (1926), for constitution of pervanadic acid.

[10] Cf. Fernandes, *Atti. accad. Lincei*, **8**, 234–8 (1928), *C.A.* **23**, 1586.

[11] Fernandes, *loc. cit.*

[12] For description and preparation of several heavy metal vanadates, see: Bleecker, *Met. Ch. Eng.*, **8**, 669–71 (1910); Ephraim, *Ahrens' Sammlung*, No. 9, p. 109–192.

7. Ignition. — Borax gives, with vanadium compounds, in the outer flame a colorless bead, yellow if much of the element be present; in the inner flame a green bead, or brown with excess and while hot, becoming green upon cooling. All the lower oxides, when ignited in air or oxygen, give V_2O_5.

8. Detection. — Since vanadium will generally be encountered as the vanadate, only that form is considered.[1] Precipitation of V_2S_5 is effected by pouring the solution of NH_4VS_3 into 6 N H_2SO_4.[2] The precipitate is dissolved and various portions of the resulting solution are tested. If an ammoniacal solution of vanadium be treated with H_2S, a violet-red color is obtained. This is a very good test in the absence of Mo.[3] Hydrogen peroxide[4] forms pervanadic acid, HVO_4, yellow to deep red, in cold, acid solution. The test is sensitive to one part in 5000. The color is not extracted by ether (distinction from Cr), or affected by H_3PO_4 (distinction from Fe^{+3}), or HF (distinction from Ti). Solid NH_4Cl yields a precipitate of NH_4VO_3, crystalline, colorless. In acid solution, metallic Zn gives a characteristic succession of colors — blue, green, violet — due to the reduction of V to V^{+4}, then V^{+3}, and finally V^{+2}. In dilute acid solution, vanadates give, with cupferron, a deep red precipitate, sensitive to one part in 250,000;[5] tannic acid gives a blue-black precipitate; strychnine sulfate in concentrated H_2SO_4 gives a blue violet, changing to a rose color. This is a very delicate test.[6]

9. Determination. — *a. Gravimetrically,* vanadium may be precipitated as $Hg_2(VO_3)_2$, ignited and weighed as V_2O_5.

b. Since the determination in steel is the one most frequently encountered, *volumetric* methods, especially those involving few if any separations, are desirable. An excellent method involving preferential oxidation (to avoid interference of Cr, etc.), is to use $KBrO_3$ in a solution containing $(NH_4)_2SO_4$ and a definite concentration of HCl. In such a medium, V is oxidized to VO_3^-, and, after removal of excess BrO_3^-, titrated with standardized $FeSO_4$. The endpoint may be determined electrometrically or by use of an internal indicator, as diphenylbenzidine.[7]

10. Oxidation and Reduction. — Vanadium reduces $HgCl_2$, $CuCl_2$ or $FeCl_3$ to the lower valence and precipitates Au, Ag and Pt from their solutions. Vanadic acid is produced by the action of ClO_3^-, ClO_4^-, BrO_3^- or IO_3^- on V°: $6\ V° + 5\ KClO_3 = 5\ KCl + 3\ V_2O_5$. The hypovanadous ion, V^{++}, is one of the strongest reducing agents known, being more active than Cr^{++}. Vanadous ion, V^{+3}, is rapidly oxidized by H_2O_2, MnO_4^-, $Cr_2O_7^{--}$, ClO_3^-, Fe^{+3}, Cl_2 or Br_2; more slowly by $S_2O_8^{--}$, Ag^+, Cu^{++}, or I_2. Hypovanadic or vanadyl compounds, V^{+4}, are rapidly oxidized by H_2O_2, MnO_4^-, $Cr_2O_7^{--}$, Cl_2, NH_2OH in alkaline solution; reduction to V^{++} is effected by Zn° in acid solution. Vanadates can be reduced to blue V^{+4} by NH_2OH, CH_2O, $H_2C_2O_4$, SO_2, H_2S, Fe^{++}, HCl, HBr, HI (PO_4^{-3} present), NO_2, H_3PO_3, $Na_2S_2O_3$, Hg°, or H_2O_2. Various metals under certain conditions give lower valences, usually a mixture. Zn°, Cd° and Al° produce an interesting succession of colors, first blue, then green, and finally lavender (i.e., V^{++}); Mg° forms V^{+3}. H_2O_2 in 15%–20% H_2SO_4 solution oxidizes vanadates to pervanadic acid, HVO_4.

[1] Cf. Friend, Vol. VI, 3, p. 109–12 (1929).

[2] Noyes and Bray, p. 72.

[3] *Ibid.*, p. 75.

[4] Lukas and Jilek, *Z. anal. Ch.*, **76**, 348–51 (1929), *C.A.* **23**, 2904, give details of procedure for detection.

[5] Turner, *Am. J. Sci.*, [4] **41**, 339 (1916); **42**, 109 (1916).

[6] Moser and Brandl, *Monatsh.*, **51**, 169–80 (1929), *C.A.* **23**, 2387, have discussed several of the tests for vanadium.

[7] Willard and Young, *Ind. Eng. Ch.*, **20**, 764 (1928). A slightly different procedure is given by Willard and Fenwick, *J. Am. Ch. Soc.*, **45**, 84 (1923).

Cf. Hillebrand and Lundell, p. 352–63; Moore, *et al.*, Bur. Mines Bull. 212, Part VII.

§174. Zirconium (Arabian *zerk* = a precious stone). Zr = 91.22. Atomic No. 40. Valence 4. Discovered by Klaproth in 1789.

1. Physical Properties. — Density, 6.5;[1] melting point, 1927°;[2] boiling point, 2900° (calc.). Two forms of metallic zirconium are now recognized. The crystalline form (about 99% pure), obtained at high temperatures, is white like white cast iron, hard and brittle. Very pure samples, however, are soft, ductile and malleable.[3] Amorphous zirconium (probably also an impure form) is a black powder. It burns when heated in air to about 500° (thin strips of the pure, ductile metal can be lighted with a match). Heated in hydrogen or nitrogen it combines to form a hydride or nitride, which in turn dissociates above 700°. The halogens combine with Zr° to form tetrahalides.[4] There is practically no demand for metallic Zr. The oxide, due to its high melting point, is used as a refractory and insulating material in high temperature work.[5] It also has been suggested as a constituent of gas mantles and glass.

2. Occurrence. — Zirconium does not occur free in nature but is found as the silicate, zircon, $ZrSiO_2$, and the oxide, baddeleyite, ZrO_2. While zircon probably is the more widely distributed, the chief commercial source is the baddeleyite deposit of the Minas Geraes district in Brazil. The commercial product contains about 74%–78% ZrO_2; the amount mined is, however, negligible. It sells for $50 to $60 per ton.

3. Preparation. — Zirconium ores may be decomposed by means of H_2SO_4 and the resulting sulfate roasted to ZrO_2.[6] Another process involves the sintering of the ore with lime and $CaSO_4$ in an electric furnace. Extraction with dilute HCl leaves calcium zirconate which is treated with concentrated H_2SO_4 to form soluble $Zr(SO_4)_2$. This is converted to the oxide as indicated above.[7]

Various methods have been proposed for the production of metallic zirconium, all being on a laboratory scale. Among the more important are: (*a*) reduction of $ZrCl_4$ with Na°; (*b*) reduction of ZrO_2 with Na° or Na° and Ca°; (*c*) reduction of K_2ZrF_6 with Na°. The last is apparently the most satisfactory for a metal of moderate purity. A purer product is obtained by conversion of Zr° to ZrI_4, followed by decomposition of the iodide.[8]

4. Oxides and Hydroxides. — The existence of zirconium monoxide, ZrO, is doubtful,[9] and of the sesquioxide, Zr_2O_3, possibly not entirely settled.[10] The dioxide, ZrO_2, white, is readily obtained by ignition of the sulfate, nitrate or hydroxide. Hauser[11] recommends the precipitation of Zr^{+4} as a basic sulfate which separates in an easily filtered form of great purity. This product is washed, dried and ignited to ZrO_2[12] which is less soluble in H_2SO_4 the higher the temperature used. The color of ZrO_2 does not change on heating (distinction from Ti and Zn); also it is less basic than TiO_2. If Zr^{+4} is treated with an alkali a white gelatinous precipitate of $ZrO_2 \cdot nH_2O$ is obtained which on standing slowly changes to $ZrO(OH)_2$. The reaction is accelerated by heat. The

[1] de Boer and Fast, *Z. anorg. allgem. Ch.*, **153**, 7 (1926). Cf. Weiss and Neumann, *Ibid.*, **65**, 248 (1910), who give 6.4.

[2] Zwicker (Cf. de Boer and Fast, *loc. cit.*).

[3] de Boer and Fast, *loc. cit.*

[4] Concerning the iodide, see de Boer and Fast, *loc. cit.*

[5] ZrO_2 melts at 2667° ± 20°, according to Henning, *Naturwissenschaften*, **13**, 661 (1925).

[6] French Pat. 654,465 (**1928**).

[7] French Pat. 650,937 (**1927**).

[8] de Boer and Fast, *Z. anorg. allgem. Ch.*, **187**, 177–84 (1930); cf. de Boer, *Ind. Eng. Ch.*, **19**, 1256 (1927); French Pat. 604,391 (**1925**).

[9] Schwartz and Deisler, *Ber.*, **52B**, 1896 (1919).

[10] Friedrich and Sittig, *Z. anorg. allgem. Ch.*, **145**, 127, 145 (1925).

[11] Hauser, *Z. anorg. allgem. Ch.*, **45**, 185, 385 (1905); **54**, 196 (1907).

[12] Cf. von Hevesy and Berglund, *J. Ch. Soc.*, **125**, 2372 (1924).

precipitate is soluble in mineral acids, practically insoluble in NaOH.[1] The higher oxide, ZrO_3, has been reported but requires further investigation.

5. Solubilities. — *a.* In general, compact Zr° is insoluble in all acids but HF and aqua regia. A mixture of HF and HNO_3 is very efficient, whereas HNO_3 alone has practically no effect. Hot, concentrated H_2SO_4 acts energetically. The alkali hydroxides react with Zr° to only a very slight extent.

b. Zirconium dioxide, when ignited, is insoluble in all acids except HF.[2] It is readily soluble in the fused caustic alkalis, forming an alkali zirconate. This product is insoluble in H_2O, being largely converted to the hydroxide by that solvent. Zirconium hydroxide is readily soluble in the common mineral acids when precipitated as $Zr(OH)_4$ from a cold solution. Precipitated from a hot solution as $ZrO(OH)_2$, it is more slowly soluble in the dilute acids, often requiring prolonged treatment (several days). In either form it is practically insoluble in H_2O, the alkalis, alkali carbonates or ammonium salts.

c. The fluorine compounds of zirconium are insoluble or difficultly soluble in H_2O. The other halide compounds are soluble but readily hydrolyzed. This hydrolysis goes so far that a solution of, e.g., $ZrOCl_2$ may be diluted with H_2O and the compound determined by titration of the HCl liberated. Zirconium nitrate is readily soluble in H_2O. The high solubility of many zirconium compounds in oxalate solution shows the close relationship of this element to thorium. In the complexes formed, Zr is in the anion.

6. Reactions.[3] — Zirconium forms three classes of salts: (1) normal Zr^{+4} compounds, as $ZrCl_4$, all of which hydrolyze readily; (2) zirconyl compounds, as $ZrOCl_2$, in which the cation, ZrO^{++}, is usually obtained by hydrolysis; (3) zirconates, theoretically derived from H_2ZrO_3 [or $ZrO(OH)_2$],[4] as Na_2ZrO_3 and $CaZrO_3$.

a. The alkali and alkaline earth hydroxides precipitate Zr^{+4} as the hydroxide, $Zr(OH)_4$, from a cold solution and $ZrO(OH)_2$ from one that is hot. The product is bulky and gelatinous, like $Al(OH)_3$. It is insoluble in excess of the reagent, any apparent solution being probably due to peptization. The fixed alkalis do not give a pure precipitate. It may be purified by solution in HCl and reprecipitation with NH_4OH. The presence of SO_4^{--} also causes trouble in that a basic sulfate may separate, which is converted to the normal hydroxide only with difficulty. The alkali carbonates precipitate Zr^{+4} as the basic carbonate, readily soluble in excess reagent,[5] and reprecipitated on boiling the solution.

b. Oxalates and tartrates precipitate Zr^{+4} as a basic salt, soluble in excess reagent. From such a solution, NaOH and $(NH_4)_2S$ do not precipitate $Zr(OH)_4$. Sodium acetate precipitates Zr^{+4} as a basic salt, which on boiling sufficiently, is completely converted to $ZrO(OH)_2$. Potassium ferrocyanide gives a green precipitate with Zr^{+4}.[6]

d. Phosphoric acid and alkali phosphates completely precipitate Zr^{+4} from strong acid solution as $ZrO(H_2PO_4)_2$.[7] The precipitate is not easily filtered.[8] In a strong HNO_3 solution containing H_2O_2, Zr and Hf are precipitated, but not Ti or Ce.[9]

e. Alkali sulfides precipitate Zr^{+4} as the hydroxide. The same is true of $Na_2S_2O_3$.[10] If SO_2 is passed into a neutral solution of Zr^{+4}, a slimy precipitate is obtained that dis-

[1] Britton, *J. Ch. Soc.*, **127**, 2133 (1925), states that zirconium hydroxide is not amphoteric.

[2] The product is $ZrF_4 \cdot 3H_2O$ (not H_2ZrF_6). Fehling, X, 604.

[3] Chauvenet and his collaborators have published a number of papers on the preparation and properties of zirconium salts in *Compt. rend.*, **164** to **167** (1917-18).

[4] See Britton, *loc. cit.*

[5] Lessing, *Z. anal. Ch.*, **67**, 341–52 (1925), suggests that the Zr is held in solution as $Zr(CO_3)_5^{-6}$.

[6] For a discussion of zirconium ferro- and ferricyanide, see: Venable and Moehlmann, *J. Am. Ch. Soc.*, **44**, 1705–7 (1922).

[7] Hevesy and Kimura, *J. Am. Ch. Soc.*, **47**, 2540–4 (1925), give the solubility of this salt as 0.0_44 g./100 cc.

[8] Cf. de Boer and van Arkel, *Z. anorg. allgem. Ch.*, **144**, 190; **148**, 84 (1926).

[9] Moser, *Monatsh.*, **45**, 323 (1925).

[10] Some investigators state that a basic thiosulfate is obtained, its composition depending on conditions.

solves on addition of excess SO_2. Sulfuric acid, added to a solution of Zr^{+4}, gives a white, flocculent precipitate, readily soluble in excess reagent and other mineral acids (separation from the rare earths and thorium). If K_2SO_4 is used a basic sulfate is obtained, insoluble in excess of the precipitant.[1] A solution of zirconium sulfate reacts toward some reagents as though a complex sulfate were present, the Zr forming a part of the anion. From such a solution oxalates do not precipitate the Zr, and sulfites very slowly produce a partial precipitation of the metal.[2]

f. By repeated fuming with HF in the presence of only a small amount of H_2SO_4, ZrO_2 may be almost completely volatilized.[3] If Zr^{+4} is treated with an iodate, a white precipitate of a basic zirconyl iodate is obtained, the composition of which depends upon conditions.[4] Sodium periodate reacts similarly.

g. Arsenic acid and soluble arsenates precipitate Zr^{+4} from strongly acid solutions, as does the phosphate ion (cf. 6, *d*).

h. Soluble chromates incompletely precipitate Zr^{+4} from weakly acid solution.[5]

7. Ignition. — Borax and microcosmic salt do not give characteristic beads with Zr^{+4},[6] nor is a distinguishing flame obtained with this element. A piece of filter paper moistened with $Co(NO_3)_2$ and a zirconium salt gives, upon charring, a blue color.[7] Zirconium hydroxide, nitrate, carbonate, sulfate and oxalate are easily converted to ZrO_2 by ignition. Fusion of the product with NaOH or Na_2CO_3 gives a zirconate of indefinite composition.[8]

8. Detection. — In the ordinary course of analysis, Zr is precipitated with the Group III metals. The hydroxides of Zr, Fe, Mn, Ti, etc., remain undissolved upon treatment with NaOH. This residue may be dissolved in concentrated HCl, the iron extracted with ether, leaving the Zr and Ti in the aqueous layer. These two elements may be separated by addition of H_2O_2 and a phosphate to precipitate the Zr (cf. 6, *d*).[9] A shorter method involves addition of a few drops of PO_4^{-3} to a sample of the original solution, strongly acidified with HCl or HNO_3. Upon warming, a gelatinous white precipitate will be obtained if as little as 0.0005% of Zr is present. Apparently no other element interferes.[10] Potassium salts give, with zirconium sulfate, a characteristic precipitate of the double salt. This is suggested as a test for potassium.[11] Turmeric paper moistened with a solution of Zr^{+4} gives a pink to red color upon drying.[12] Boric acid and Ti interfere. Pyrogallol aldehyde gives a yellow color with Zr^{+4}. Upon boiling the solution a dirty yellow precipitate and a colorless filtrate are obtained. Thorium interferes.[13] Zirconium yields colored complex salts with β-naphthol and β-nitroso-α-naphthol,[14] with alizarin sulfonic acid a violet-red color is obtained that turns to yellow on addition of a small amount of fluoride. The test will detect 0.001 mg. of Zr per cc. of solution. Hafnium is the only element that interferes.[15] A number of other tests involving organic reagents have been described by Pavelka.[16]

[1] Cf. 8 and §205.

[2] Ruhr, *Z. anorg. allgem. Ch.*, **42**, 85 (1904); Britton, *J. Ch. Soc.*, **127**, 2137 (1925).

[3] Wedekind, *Ber.*, **44**, 1753–5 (1911), *C.A.* **5**, 3205.

[4] Venable and Smithy, *J. Am. Ch. Soc.*, **41**, 1722 (1919); Davis, *Am. Ch. J.*, **11**, 26 (1889).

[5] Venable and Giles, *J. Am. Ch. Soc.*, **40**, 1653 (1918).

[6] Wunder, *J. prakt. Ch.*, [2] **109**, 475 (1870).

[7] Miglineci and Crapetta, *Ann. ch. anal. ch. appl.*, **17**, 66 (1927).

[8] Fehling, X, 613.

[9] Noyes, *et al.*, *J. Am. Ch. Soc.*, **30**, 481 (1908); Noyes and Bray, pp. 148, 206.

[10] Biltz and Mecklenburg, *Z. angew. Ch.*, **25**, 2110 (1912).

[11] §205. Cf. Reed and Withrow, *J. Am. Ch. Soc.*, **50**, 1515, 2985 (1928); **51**, 1062 (1929).

[12] Brush, *Am. J. Sci.*, [2] **18**, 415 (1854).

[13] Kaserer, *Ch. Ztg.*, **42**, 170, 291 (1918), *C.A.* **12**, 2174; **13**, 3111.

[14] Bellucci and Savola (*C.A.* **18**, 3333).

[15] de Boer, *Ch. Weekblad*, **21**, 404 (1924); Basart, *Z. anorg. allgem. Ch.*, **152**, 213 (1926).

[16] Pavelka, *Mikrochemie*, [n.s.] **2**, 345–51 (1930), *C.A.* **25**, 892.

9. Determination. — Zirconium may be separated from most of the other elements by precipitation with a phosphate in strong acid solution. The precipitate is washed, ignited to ZrP_2O_7 and weighed as such. When used for large amounts of Zr, the method tends to give low results due to hydrolysis and consequent loss of phosphate. The interference of Ti may be prevented by addition of H_2O_2. This also helps with Cb and Ta, but the precipitate must be purified.[1]

Cupferron may be used for the separation of zirconium (in H_2SO_4 solution) from Al, Cr, U^{+6}, BO_3^{-3} and small amounts of phosphate. The precipitate, $Zr(C_6H_5N_2O_2)_4$, is ignited to ZrO_2 and weighed.[2]

When the analysis of zirconium salts is involved, precipitation as the hydroxide with NH_4OH and subsequent ignition to ZrO_2 is a very satisfactory procedure.[3]

THE CALCIUM GROUP (FIFTH GROUP)

(THE ALKALINE EARTH METALS)

BARIUM, STRONTIUM AND CALCIUM (MAGNESIUM)

§186. Barium (Gr. *barys* = heavy). Ba = 137.36. Atomic No. 56. Valence 2. First prepared by Davy in 1808.

1. Physical Properties. — Density 3.5 at 25°/4°;[4] melting point, 850°;[5] boiling point, 1140°.[6] Barium is a silvery white metal, stable in dry air, but readily oxidized in moist air or in H_2O at room temperature, H_2 being evolved and $Ba(OH)_2$ formed. It is malleable and ductile, slightly harder than Pb°. The metal burns brilliantly when heated in air to form the peroxide. It is volatile in a vacuum. Soluble barium salts are very poisonous.

2. Occurrence. — The chief ore is barite or heavy spar, $BaSO_4$; of secondary importance is witherite, $BaCO_3$. These minerals are fairly widely scattered, but in the United States — because of the cost factor — barite is mined principally in Georgia, Missouri, Tennessee and California. The first two states mentioned produce about 80% of the total — 350,000 tons in 1930. The most important use of barite is in lithopone paint. Only a very small amount is reduced to the metal which is used as a " getter " in radio tubes, and alloyed with Ni, as a material for ignition systems in automobiles. The price is about $35 per pound.

3. Preparation. — As indicated above, barite is used largely as mined. The small amount of metal produced is probably obtained by electrolysis[7] of the fused chloride. This product is said to be over 99.9% pure.

[1] Hillebrand and Lundell, 444–5.

[2] Thornton and Hayden, *Am. J. Sci.*, [4] **38**, 137 (1914); Lundell and Knowles, *Ind. Eng. Ch.*, **12**, 344 (1920); *J. Am. Ch. Soc.*, **42**, 1439 (1920); Hillebrand and Lundell, 448.

[3] For other separations, see: Rüdisüle, VI, 999–1033.

[4] Biltz and Hüttig, *Z. anorg. allgem. Ch.*, **114**, 247 (1920).

[5] B. Stds. Cir. 35; cf. Hartmann and May, *Z. anorg. allgem. Ch.*, **185**, 167–71 (1929).

[6] Cf. Hartmann and May, *Ibid.*

[7] Cf. Guntz, *Chimie & industrie*, Special No., Feb. 1929, p. 458–62, *C.A.* **23**, 3638; Dannar, *J. Am. Ch. Soc.*, **46**, 2382 (1924); Matignon, *Compt. rend.*, **177**, 1116 (1923).

4. Oxides and Hydroxides. — Barium oxide, BaO, white, is obtained by ignition of the hydroxide, carbonate, nitrate, oxalate and all of its organic salts. The hydroxide, $Ba(OH)_2$, is made by treating the oxide with H_2O. The peroxide BaO_2 is formed when the oxide is heated to 500°–600° in oxygen.[1] Conversion is approximately 70% complete when heated in air to about 500°. Decomposition to $BaO + O_2$ takes place around 900°. Treatment of BaO_2 with an acid produces H_2O_2.

5. Solubilities. — *a. Metal.* — Barium reacts with H_2O to form $Ba(OH)_2$ at room temperature. It is readily soluble in acids with evolution of hydrogen.

b. Oxides and Hydroxide. — Barium oxide reacts with water ("slakes") with evolution of heat and formation of $Ba(OH)_2$, which dissolves to the extent of about 3 g./100 cc. at room temperature and in its own weight of hot water. Barium peroxide, BaO_2, is insoluble in H_2O, soluble in acids with formation of H_2O_2.

c. Salts. — Most of the soluble salts of Ba are stable; the acetate, however, is efflorescent. The acetate, chloride, chlorate, perchlorate, bromide, iodide and cyanide are readily soluble; the ferrocyanide and nitrate moderately soluble; the fluoride slightly soluble; the oxalate, sulfite, sulfate, chromate, phosphate, carbonate and iodate insoluble. The sulfate is perceptibly soluble — the chloride is almost insoluble — in concentrated HCl. The nitrate is quite insoluble in concentrated HCl or HNO_3. The chloride and nitrate are insoluble in alcohol.

6. Reactions. — *a.* The fixed alkali hydroxides (free from CO_3^{--}) precipitate Ba^{++} only from fairly concentrated solutions. Since NH_4OH furnishes a lower $[OH^-]$ than $Ba(OH)_2$ no precipitate is obtained with that reagent. The alkali carbonates precipitate barium carbonate, $BaCO_3$, white.[2] Precipitation is promoted by heat, but excess of ammonium salts prevents complete separation due to their tendency to hydrolyze, raise the acidity of the solution and promote formation of soluble $Ba(HCO_3)_2$. In addition there is, of course, the mass action effect.

b. Soluble oxalates precipitate Ba^{++} as barium oxalate, $BaC_2O_4 \cdot H_2O$, white, soluble in HCl and HNO_3. When first precipitated this compound may be dissolved in acetic or oxalic acid, but in a short time $H_2Ba(C_2O_4)_2 \cdot 2H_2O$ separates in the form of clear crystals.

c. Solutions of Ba^{++} yield a fairly coarse, crystalline precipitate when treated with HNO_3 (cf. 5, *c*).

d. Soluble secondary and tertiary phosphates precipitate barium phosphate: Na_2HPO_4 gives $BaHPO_4$; Na_3PO_4 forms $Ba_3(PO_4)_2$. Soluble phosphites precipitate Ba^{++}, but hypophosphites do not.

e. Solutions of Ba^{++} treated with an alkaline sulfide give a white precipitate, possibly $Ba(HS)_2$.

Soluble sulfites precipitate Ba^{++} as barium sulfite, $BaSO_3$, white, insoluble in water but soluble in HCl (distinction from the sulfate).

[1] Friend, III, 1, 223.

[2] Positive Group III ions, except Fe^{++}, are precipitated as hydroxides by $BaCO_3$, while the ions of Group IV, in a chloride solution, are not affected. Tartaric or citric acid, sugar and other organic compounds hinder or prevent the separation.

All soluble sulfates precipitate Ba^{++} as barium sulfate, $BaSO_4$, white, slightly soluble in hot concentrated H_2SO_4[1] (cf. 5, *c*).

Immediate precipitation by a saturated solution of $CaSO_4$ distinguishes Ba^{++} from Sr^{++}, but precipitation by a solution of $SrSO_4$ (very dilute, due to its low solubility) offers a more certain distinction. Boiling $BaSO_4$ with at least fifteen times its equivalent weight of 2–4 *N* Na_2CO_3 will convert 99% of the $BaSO_4$ to Na_2SO_4 in one hour, in the case of a fresh precipitate. About double the time is required for native barite.[2] Filtration and digestion with H_2O will remove any soluble sulfate after which the $BaCO_3$ residue may be dissolved in HCl.

f. Iodate solutions precipitate Ba^{++} as barium iodate, $Ba(IO_3)_2 \cdot H_2O$, white, soluble at room temperature to the extent of 0.028 g./100 cc. of solution (distinction from the other alkaline earth metals).[3]

g. Neutral or ammoniacal solutions of arsenious acid do not precipitate Ba^{++} (distinction from Ca). Soluble arsenates precipitate Ba^{++} as $BaHAsO_4 \cdot H_2O$, white, slightly soluble in H_2O, soluble in acids.

h. Soluble chromates or dichromates[4] precipitate Ba^{++} as barium chromate, $BaCrO_4$, yellow, insoluble in H_2O (separation from Sr and Ca except in concentrated solutions), sparingly soluble in acetic acid, readily soluble in HCl and HNO_3.[5]

i. Fluosilicic acid, H_2SiF_6, precipitates white crystalline barium fluosilicate, $BaSiF_6$, slightly soluble in H_2O, insoluble in alcohol (distinction from Sr and Ca). If an equal volume of alcohol is added precipitation of Ba^{++} is complete, H_2SO_4 not giving a precipitate in the filtrate;[6] Na^+ and K^+ interfere with this test.

7. Ignition. — The volatile salts of Ba, e.g., $BaCl_2$,[7] impart a green color to the flame of a Bunsen burner. The spectrum of Ba is readily distinguished from the spectra of other metals by the green bands: Ba α (524mμ), β (513.2mμ), and δ (553.5mμ). Barium carbonate is very stable when heated, requiring a temperature of about 1350° to decompose it into BaO and CO_2.[8] Fusion of $BaSO_4$ with Na_2CO_3 completely converts the barium to $BaCO_3$.

[1] Meyer and Friedrich, *Z. physik. Ch.*, **101**, 498 (1922).

[2] Wolesensky, *Ind. Eng. Ch., Anal. Ed.*, **1**, 29–31 (1929).

[3] Benedict, *J. Am. Ch. Soc.*, **28**, 1596–8 (1906).

[4] $K_2Cr_2O_7 \rightleftarrows 2\,K^+ + Cr_2O_7^{--}$

$Cr_2O_7^{--} + H_2O \rightleftarrows 2\,HCrO_4^-$

$HCrO_4^- \rightleftarrows H^+ + CrO_4^{--}$

$CrO_4^{--} + Ba^{++} \rightleftarrows BaCrO_4$

If the solution is sufficiently buffered to take care of the H^+ released, precipitation will be complete.

[5] Waddell, *Analyst*, **43**, 287–9 (1918), *C.A.* **12**, 2175, has studied the solubility of $BaCrO_4$ in various aqueous solutions.

[6] Caron and Raquet, *Bull. soc. ch.*, [4] **3**, 483 (1908).

[7] Krauss, *Ch. Ztg.*, **50**, 33 (1926), **51**, 38 (1927), has advocated the use of $BaSO_4$.

[8] Johnston, *J. Am. Ch. Soc.*, **30**, 1357 (1908); Hedvall, *Z. anorg. allgem. Ch.*, **98**, 53 (1916).

8. Detection. — *a.* In the Group IV filtrate, freed from excess NH_4^+, the Ba^{++} is precipitated by $(NH_4)_2CO_3$[1] as $BaCO_3$ along with $SrCO_3$ and $CaCO_3$. The precipitate is dissolved in acetic acid, sodium acetate added, and the Ba^{++} separated from Sr^{++} and Ca^{++} by precipitation as $BaCrO_4$. The yellow precipitate is dissolved in HCl and portions of the resulting solution may be treated with SO_4^{--} to obtain $BaSO_4$ or tested with a flame to secure a green color.[2]

b. Very few organic reagents have been suggested for the detection or differentiation of Ba, Sr and Ca.[3]

9. Determination. — Where possible Ba^{++} is always precipitated and weighed as $BaSO_4$. If only Group V ions[4] are present, Ba^{++} may be precipitated as $BaCrO_4$ and weighed as such. The formation of this compound may also be the basis for the volumetric determination of barium.

10. Oxidation and Reduction. — Considering its insolubility in water, BaO_2 acts as a normal peroxide (see hydrogen peroxide, §244). Metallic Ba is a powerful reducing agent, similar in action to alkali metals.

§187. Strontium (*Strontian*, a town in Scotland). Sr = 87.63. Atomic No. 38. Valence 2. Isolated by Davy in 1808.

1. Physical Properties. — Density, 2.6;[5] melting point, 752° ± 2°;[6] boiling point, 1639° ± 5°.[7] Strontium is a silvery white metal, malleable and ductile. Its hardness is about that of lead. It oxidizes rapidly when exposed to the air, and when heated burns, like barium, with intense illumination. The chief uses are: as $Sr(OH)_2$ in the beet sugar industry, and as $Sr(NO_3)_2$ in fireworks to produce a red flame. A small amount of the carbonate is used in the preparation of iridescent glass.[8]

2. Occurrence. — Strontium occurs chiefly as celestite, $SrSO_4$, and strontianite, $SrCO_3$. It is rather widely distributed but the only deposits commercially exploited are those in England. The metal has been commercially available since 1929 but there is practically no demand for it. In recent years the United States has imported annually over three million pounds of strontium chemicals and ores.

3. Preparation. — Strontium may be obtained by electrolysis of $SrCl_2$, using a mercury cathode. The amalgam thus obtained is heated in hydrogen to drive off the Hg.

[1] $BaCO_3$ precipitates slowly from dilute solutions. Also, Curtman and Frankel, *J. Am. Ch. Soc.*, **33**, 724 (1911), state that in ordinary qualitative analysis it is impossible to detect small amounts of Ba^{++} because of the losses occurring in previous steps.

[2] Lutz, *Z. anal. Ch.*, **60**, 209 (1921), *Analyst*, **47**, 93 (1922), discusses the delicacy of the various tests for Ba^{++}, stating that the most sensitive reagent for Ba^{++} is the sulfate ion, while the chromate ion is almost as sensitive. A summarizing table is given in Rüdisüle, VI, 2, p. 1806–9.

[3] Gutzeit, *Helv. Ch. Acta*, **12**, 713–40 (1929), *C.A.* **23**, 4644–5.

[4] Hillebrand and Lundell, p. 490, state, however, that no really good methods for separating calcium, strontium and barium from each other have been described.

[5] King, *Proc. Natl. Acad. Sci.*, **15**, 337–8 (1929).

[6] Hartmann and May, *Z. anorg. allgem. Ch.*, **185**, 167–71 (1929), *C.A.* **24**, 1264.

[7] Hartmann and Schneider, *Z. anorg. allgem. Ch.*, **180**, 275–83 (1929), *C.A.* **23**, 4383.

[8] Santmyers, Bur. Mines Ec. Paper No. 4, gives a good survey of the strontium industry.

Another method involves the reduction of SrO with Al° in a vacuum at 1000°. The metallic Sr crystallizes in needles 99+% pure.[1]

4. Oxides and Hydroxides. — Strontium oxide, SrO, white, is formed by igniting the hydroxide, carbonate (higher temperature required than in case of $CaCO_3$), nitrate, and all organic strontium salts. The hydroxide, $Sr(OH)_2$, is formed by the action ("slaking") of water on the oxide or by heating the carbonate in steam: $SrCO_3 + H_2O = Sr(OH)_2 + CO_2$. Strontium peroxide, $SrO_2 \cdot 8H_2O$, is made by treating $Sr(OH)_2$ with H_2O_2. The oxide is not readily converted to the peroxide by heating in air (distinction from Ba).

5. Solubilities. — *a. Metal.* — Strontium decomposes H_2O at room temperature, and is soluble in acids with evolution of hydrogen.

b. Oxides and Hydroxide. — The oxide, SrO, dissolves in water at room temperature to the extent of about 0.7 g./100 cc. of solution.[2] There is an abnormal decrease in solubility in the presence of other bases. The peroxide, $SrO_2 \cdot 8H_2O$, is only slightly soluble in water or NH_4OH but is soluble in acids and in NH_4Cl.

c. Salts. — The chloride is slightly deliquescent; crystals of the nitrate and acetate are efflorescent. The chloride is soluble, the nitrate insoluble in absolute alcohol. The nitrate is insoluble in boiling amyl alcohol. The sulfate is practically insoluble in H_2O (0.01 g./100 cc. solution at 20°) yet enough dissolves to allow its use as a reagent for traces of barium. $SrSO_4$ is less soluble in solutions of $(NH_4)_2SO_4$, Na_2SO_4, or H_2SO_4[3] than in H_2O; it is appreciably soluble in HCl or HNO_3, insoluble in alcohol.[4] The fluosilicate is soluble in H_2O (distinction from Ba). The chromate dissolves in H_2O to the extent of 0.11 g./100 cc. of solution at 15°. It is soluble in many acids, including chromic, and more soluble in a concentrated solution of NH_4^+ than in water. The oxalate is soluble in H_2O to the extent of 0.006 g./100 cc. of solution at 20°.

6. Reactions. — *a.* The fixed alkalis precipitate Sr as $Sr(OH)_2$, from solutions not too dilute. This compound is less soluble than $Ba(OH)_2$. No precipitate is obtained with NH_4OH (§186, 6, *a*). The alkali carbonates precipitate Sr^{++} as $SrCO_3$.

b. Oxalic acid, i.e., $C_2O_4^{--}$, precipitates strontium oxalate, SrC_2O_4, insoluble in H_2O, soluble in HCl or HNO_3. Alkali ferrocyanides do not precipitate Sr^{++}.

c. The solubility of $Sr(NO_3)_2$ is diminished by the presence of HNO_3, but less so than in the case of Ba.

d. In reactions with phosphates, Sr is not to be distinguished from Ba.

e. Alkali sulfides precipitate Sr^{++} possibly as $Sr(HS)_2$, white, from solutions not too dilute. Sulfite ion precipitates Sr^{++} as $SrSO_3$, white, from neutral or acetic acid solutions of Sr^{++}. The precipitate is readily soluble in HCl. Sulfuric acid, i.e., SO_4^{--}, precipitates Sr^{++} as strontium

[1] Dannar, *J. Am. Ch. Soc.*, **46**, 2382 (1924). Guntz and Galliot, *Compt. rend.*, **151**, 813 (1910).

[2] Cf. Sidersky, *Bull. assoc. ch. sucr. dist.*, **39**, 167–77 (1921), *C.A.* **16**, 2435.

[3] $SrSO_4$ is soluble in concentrated H_2SO_4: $SrSO_4 + H^+ \rightarrow Sr^{++} + HSO_4^-$.

[4] Cf. Lutz, *Z. anal. Ch.*, **60**, 433 (1921).

sulfate, $SrSO_4$, unless the solution is too dilute.[1] A solution of $SrSO_4$ may be used to detect the presence of traces of Ba^{++}. In dilute solutions $SrSO_4$ separates very slowly. Precipitation is aided by boiling or by addition of alcohol, prevented by the presence of HCl, HNO_3, Ca^{++} (in high concentration and other polyvalent metal ions). Boiling in a solution of fixed alkali carbonate converts $SrSO_4$ to $SrCO_3$ far more readily than $BaSO_4$ is transposed (§186, 6, *e*).

f. Concentrated solutions of Sr^{++} give a precipitate of $Sr(IO_3)_2$ with iodate ion; the more dilute the solution the slower the separation. (Solubility: 0.3 g./100 cc. of solution at room temperature.)

g. Neutral solutions of arsenites do not precipitate Sr^{++}. The addition of NH_4OH causes a portion of the Sr^{++} to precipitate. Strontium arsenate resembles the corresponding Ba salt. Alkali arsenates do not precipitate Sr^{++} from a solution of $SrSO_4$ (distinction from Ca).

h. Normal chromates precipitate strontium chromate, $SrCrO_4$, from solutions sufficiently concentrated. The precipitate is soluble in acids. In absence of Ba^{++} strontium may be separated from Ca^{++} by adding CrO_4^{--} to the nearly neutral solution containing one-third alcohol or acetone. At room temperature $CaCrO_4$ is about twenty times more soluble than $SrCrO_4$. Dichromates give no precipitate with Sr^{++}.

i. Fluosilicic acid does not precipitate Sr^{++} even from quite concentrated solutions, especially in the presence of HCl.

7. **Ignition.** — Volatile Sr compounds color the Bunsen flame crimson. In presence of Ba the Sr color appears when the substance is first placed in the flame. The paler yellow-red flame of Ca is likely to be confused with the Sr flame. The spectrum of Sr is characterized by eight bright bands: six red, one orange, and one blue. The orange line *Srα* (605.5mμ) at the red end of the spectrum, the two red lines, *Srβ* (679.7mμ) and *Srγ* (649.9mμ), and the blue line, *Srδ* (460.7mμ), are the most important. The last (especially) identifies Sr in the presence of Ca and Ba.

8. **Detection.** — Ammonium carbonate precipitates Sr^{++}, Ba^{++} and Ca^{++} from the slightly ammoniacal Group IV filtrate, excess NH_4^+ having been removed previously. The carbonate precipitate is dissolved in acetic acid and the Ba^{++} removed as $BaCrO_4$.[2] The Sr^{++} and Ca^{++} are separated from excess CrO_4^{--} by reprecipitation with $(NH_4)_2CO_3$. The precipitate is dissolved in $HC_2H_3O_2$, and, from a portion of the solution, the Sr^{++} is removed as $SrSO_4$ with $CaSO_4$.[3] (Cf. §192, note 7.) The precipitate is moistened with HCl and the flame test applied.[4]

[1] For the effect of various factors see Lambert and Hume-Rothery, *J. Ch. Soc.*, **1926**, 2637–48.

[2] For separation of Ba, Sr and Ca by the chromate method see Kolthoff, *Pharm. Weekblad*, **57**, 1080–4 (1920), *C.A.* **14**, 3381.

[3] Raikow, *Z. anal. Ch.*, **57**, 164–70 (1918), *C.A.* **12**, 2293.

[4] Cf. Gutzeit, *Helv. Ch. Acta*, **12**, 713–40 (1929), *C.A.* **23**, 4644; Kolthoff, *Pharm. Weekblad*, **62**, 1017–20 (1925), *C.A.* **20**, 158; Lutz, *Z. anal. Ch.*, **60**, 433 (1921), *C.A.* **16**, 880. Rüdisüle, VI, 2, 1812–3.

9. Determination. — After separation from the other alkaline earth metals[1] strontium may be precipitated and weighed as the sulfate or oxalate.[2] *Volumetrically*, the oxalate may be titrated with $KMnO_4$ or the chromate may be precipitated and treated as is $BaCrO_4$.

§188. Calcium (L. *calx* = lime). Ca = 40.08. Atomic No. 20. Isolated by Davy in 1808.

1. Physical Properties. — Density, 1.545 at 25°;[3] melting point, 810°;[4] boiling point, 1712° ± 5°.[5] Calcium is a silvery white metal resembling aluminum. It is distinctly volatile at the melting point, is somewhat malleable and ductile, and is slightly harder than lead. In dry air it is quite stable; in moist air or in the halogens it burns with incandescence. It dissolves in Hg, forming an amalgam. Calcium metal is not used to any great extent. Probably the principal commercial alloy is Pb-Ca (0.04% Ca) in which the Ca acts as a hardener. The alloy is believed to be more satisfactory than pure Pb as a sheathing for electric cables. Limestone, marble, and gypsum building materials various forms of agricultural lime, $CaCO_3$ for glass, and limestone for metallurgical purposes, are the chief commercial forms.

2. Occurrence. — Metallic calcium is not found native, but in compounds it is widely distributed, comprising about 3.5% of the earth's crust. The principal ores are calcium carbonate, as calcite, aragonite, and dolomite; calcium sulfate, as gypsum, $CaSO_4 \cdot 2H_2O$; calcium fluoride, or fluorite, CaF_2; and calcium phosphate-fluoride, $Ca_5F(PO_4)_3$, or apatite. Calcium is found as a phosphate in bones, as a carbonate in egg shells and oyster shells. It is found in nearly all spring and river waters. In the United States, accounting for about half of the world's production, the leading sources of limestone are: Pennsylvania, Ohio, Indiana, New York and Michigan. The principal sources of gypsum are New York, Michigan and Iowa. In 1929 New York produced about 1.3 million tons of gypsum which was 26% of the total mined in the entire country that year.[6] The value of the total gypsum sold by producers, was 31.3 million dollars; probably all calcium minerals totaled over four times that value.[7]

3. Preparation. — Calcium has been produced by reduction of its compounds and displacement by more electro-positive metals. Probably the most important method is electrolysis of the fused chloride with or without the addition of another compound, e.g., CaF_2, to reduce the temperature of fusion. Anhydrous $CaCl_2$ is placed in a graphite crucible, then fused, and an iron cathode, in contact with the upper surface of the liquid, is slowly raised, removing from the bath metallic calcium in the form of a rod coated with the electrolyte. The working temperature is 650°–700° because the metal ignites at about 800°. A product 98%–99% pure may be obtained.[8]

4. Oxides and Hydroxides. — The oxide, CaO, is strongly basic, distinctly volatile above 2000°, and fuses at a somewhat higher temperature (over 2500°). It is, however, very refractory as demonstrated by its use in the Drummond or lime light where it withstands the intense heat of the oxy-hydrogen flame. Calcium oxide is formed by oxidation of the metal in air; by ignition of the hydroxide, carbonate (limestone), nitrate and all organic calcium salts. In case of the carbonate decomposition starts above 600°, and

[1] Richards and Yngve, *J. Am. Ch. Soc.*, **40**, 91 (1918).

[2] Hillebrand and Lundell, p. 503–4.

[3] Biltz and Wagner, *Z. anorg. allgem. Ch.*, **134**, 4 (1924).

[4] B. Stds. Cir. 35. Hartmann and May, *Z. anorg. allgem. Ch.*, **185**, 167–71 (1929), *C.A.* **24**, 1264.

[5] Hartmann and Schneider, *Ibid.*, **180**, 275–83 (1929), *C.A.* **23**, 4383.

[6] Mineral Ind., **1929**, p. 319.

[7] Mineral Resources of the U.S., **1929**, 2, p. 229–54.

[8] Brace, *Trans. Am. Electroch. Soc.*, **37**, 465 (1920), deals chiefly with the commercial preparation.

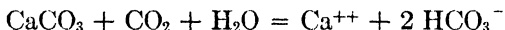
the CO_2 pressure equals that of the atmosphere at 910°.[1] This reaction is the basis for the ancient process known as lime burning,[2] and is still extensively used for the preparation of quicklime. The hydroxide, $Ca(OH)_2$ (slaked lime), is made by treating the oxide with water. Its usefulness when combined with sand, making mortar, is well known. The peroxide, $CaO_2 \cdot 8H_2O$ is made by adding H_2O_2 or Na_2O_2 to the hydroxide: $Ca(OH)_2 + H_2O_2 = CaO_2 + 2\,H_2O$. Careful dehydration of $CaO_2 \cdot 8H_2O$ by heating leaves CaO_2. It cannot be obtained by heating the oxide in O_2 or with $KClO_3$.

5. Solubilities. — *a. Metal.* — Calcium decomposes water, evolving H_2 and forming $Ca(OH)_2$. The same type of reaction takes place still more readily with acids.[3]

b. Oxides and Hydroxides. — Calcium oxide combines with dilute acids to form the ions of the corresponding calcium salt. It absorbs CO_2 from the air, becoming $CaCO_3$. In moist air it becomes $Ca(OH)_2$, the reaction taking place rapidly, with increase in volume and generation of much heat if sufficient water is present. The hydroxide, $Ca(OH)_2$, reacts with acids to form H_2O and the ions of the corresponding salts. It is much less soluble in H_2O than $Ba(OH)_2$ or $Sr(OH)_2$ — 1.198 g./l. of saturated solution[4] at 30°. It dissolves with evolution of heat, the solubility decreasing with an increase in temperature, being about two-thirds of the quoted figure at the boiling point. A clear solution of the hydroxide in water is known as lime water while a suspension of creamy consistency is called milk of lime.

c. Salts. — The chloride, bromide, iodide, nitrate and chlorate are deliquescent; the acetate is efflorescent. The carbonate, oxalate, phosphate, and fluoride[5] are insoluble in H_2O. The chloride, iodide and nitrate are soluble in alcohol. The nitrate is soluble in a mixture of equal parts of ether and alcohol; it is readily soluble in boiling amyl alcohol (separation from Ba and Sr).

The *carbonate* is soluble in water containing an excess of CO_2 due to the formation of HCO_3^-:

$$CaCO_3 + CO_2 + H_2O = Ca^{++} + 2\,HCO_3^-$$

The same is true of the other alkaline earth carbonates. In other words, although their carbonates are insoluble, their bicarbonates readily dissolve in H_2O. This is one of the important factors in the "temporary" hardness of water. Due to the fact that oxalic acid is more highly ionized than acetic, calcium oxalate is insoluble in the latter but readily soluble in HCl, HNO_3 and H_2SO_4. The sulfite, $CaSO_3 \cdot 2H_2O$, is slightly soluble in H_2O. The *sulfate*, $CaSO_4 \cdot 2H_2O$, i.e., gypsum, dissolves to the extent of 0.208 g./100 cc. of solution at 25°. The value changes but slightly up

[1] The corresponding Ba and Sr salts remain unaltered in that range. Hence $CaCO_3$, alone, can be completely decomposed by removal of the CO_2 as formed. (Raikow, *Ch. Ztg.*, **40**, 781 (1916), *C.A.* **11**, 924.)

[2] The Egyptians before 2700 B.C. "burned" gypsum extensively (forming plaster of Paris, not CaO) because of the lower temperature required and the scarcity of fuel.

[3] Ca° is only slightly attacked by concentrated HNO_3 due, possibly, to the formation of a protective coating of calcium nitrate insoluble in the acid.

[4] Miller and Witt, *J. Phys. Ch.*, **33**, 285 (1929). They used gravimetric and electrical conductivity methods.

[5] Karaoglanow, *Z. anal. Ch.*, **56**, 138 (1917), *C.A.* **11**, 2869, uses a solution of BaF_2 to detect Ca^{++}. He gives the following solubility values per 100 cc.:
CaF_2 – 0.0016 g.; SrF_2 – 0.0117 g.; BaF_2 – 0.163 g.

to 100°; from there to about 200° the decrease is comparatively rapid, an important factor in the problem of boiler scale. The solubility of $CaSO_4 \cdot 2H_2O$ in most alkali salts is greater than in pure water, in fact it is readily soluble in hot $(NH_4)_2SO_4$[1] or in a solution of $Na_2S_2O_3$. In alcohol it is almost insoluble but in acids (HCl and HNO_3) its solubility is much greater than in H_2O. The chromate, $CaCrO_4$, dissolves to the extent of 2.3 g./100 cc. of aqueous solution. It is somewhat more soluble in alcohol, readily soluble in acids including chromic acid.

6. **Reactions.** — *a.* The fixed alkali hydroxides precipitate Ca from solutions sufficiently concentrated (NaOH will precipitate $Ca(OH)_2$ from a solution of $CaSO_4$, the hydroxide being less soluble especially in the presence of excess reagent). No precipitate is obtained with NH_4OH free from CO_3^{--}. Alkali carbonates precipitate Ca^{++} as calcium $CaCO_3$, insoluble in CO_2-free water (see p. 405), decomposed by acids. Calcium hydroxide may be used as a reagent for the detection of carbon dioxide but it should be noted that excess CO_2 causes the precipitate of $CaCO_3$ to dissolve (see above).

b. Solutions of oxalate ion, $C_2O_4^{--}$, quantitatively precipitate Ca^{++} as $CaC_2O_4 \cdot H_2O$. The precipitate is readily soluble in mineral acids, quite insoluble in acetic acid (see above). Precipitation is best effected by addition of dilute NH_4OH to a hot acid solution containing both Ca^{++} and $HC_2O_4^-$. If Sr^{++} or Ba^{++} is present in the solution to be tested (qualitatively), $(NH_4)_2SO_4$[2] should first be added. After digesting, any precipitate that appears is removed by filtration and the oxalate test applied to the filtrate.

Excess potassium ferrocyanide precipitates, from solutions of Ca^{++}, $CaK_2Fe(CN)_6$, white.[3] An excess of NH_4Cl is also necessary.[4] The test is said to be more delicate in the presence of $RbNO_3$ or $CsNO_3$, and most sensitive if alcohol is present.[5] Magnesium interferes.

d. Solutions of Ca^{++} are not distinguished from Ba^{++} or Sr^{++} by the action of alkali phosphates. From a neutral solution of Ca^{++} (or Ba^{++} or Sr^{++}) Na_2HPO_4 precipitates $CaHPO_4$, white. If NH_4OH is present the product is $Ca_3(PO_4)_2$.

e. The sulfide ion, in moderately to strongly alkaline solution, precipitates Ca^{++} as CaS, white, granular (solubility 0.0212 g./100 cc. at 20°). The acid sulfide ion, HS^-, does not precipitate Ca^{++}. Hydrogen sulfide

[1] With K_2SO_4 it forms a double salt whose solubility decreases with increasing K_2SO_4 concentration.

[2] Not K_2SO_4 as is usually suggested, because it forms an insoluble double salt with $CaSO_4$.

[3] Baubigny, *Bull. soc. ch.*, [3] **13**, 326 (1895).

[4] In presence of the ammonium salt the composition of the precipitate varies.

[5] Murmann, *Oesterr. Ch. Ztg.*, **28**, 42–4 (1925), *C.A.* **19**, 1827. Cf. Feigl and Pavelka, *Mikrochemie*, **2**, 85–91 (1924).

causes solution of CaS, due to the formation of $Ca(HS)_2$ which is readily soluble (20.65 g./100 cc. at 20° and a pressure of H_2S of one atmosphere).[1] Alkali sulfites precipitate Ca^{++} as calcium sulfite, $CaSO_3 \cdot 2H_2O$, nearly insoluble in water, soluble in HCl, HNO_3, or H_2SO_3.[2] Solutions of SO_4^{--} precipitate Ca^{++} as $CaSO_4$ from systems not too dilute.[3] This compound is distinguished from $BaSO_4$ by its solubility in H_2O and HCl, and by the ease of conversion to the carbonate upon boiling with a solution of Na_2CO_3. An aqueous solution of $CaSO_4$ is occasionally used to detect Sr^{++} after the removal of Ba^{++}.

f. Solutions of soluble fluorides precipitate Ca^{++} as CaF_2 (cf. 4).

g. Neutral or ammoniacal solutions of AsO_3^{-3} form a precipitate with Ca^{++}. The same is true of the arsenate ion.[4]

h. Normal chromates, K_2CrO_4, precipitate Ca^{++} as $CaCrO_4$, yellow, provided the solution is sufficiently concentrated. The precipitate is readily soluble in acids. Ammonium molybdate precipitates Ca from a slightly alkaline solution as $CaMoO_4$, insoluble in H_2O (separation from Mg).[5] Sodium tungstate completely precipitates Ca^{++} as $CaWO_4$ (separation from Mg^{++}).[6]

i. Fluosilicic acid does not precipitate Ca^{++} even in the presence of an equal volume of alcohol (separation from Ba^{++}).

7. Ignition. — Calcium sulfate dihydrate loses 1.5 H_2O slightly below 100°. The hemihydrate, $CaSO_4 \cdot \frac{1}{2}H_2O$, begins to decompose at about 180°. Further heating gives the insoluble form of $CaSO_4$.[7] Calcium carbonate (limestone), when heated around 900°, loses CO_2[8] and becomes quicklime, CaO.

Volatile compounds of Ca, e.g., $CaCl_2$, render the Bunsen flame yellowish red. The presence of Sr^{++}, Ba^{++}, or Na^+ obscures the color. It is claimed by some workers that Ca^{++} can be detected because it gives the characteristic color on its first introduction into the flame while the others are slower to appear. The spectrum of Ca is distinguished by the bright green line Caβ (554.4mμ), and the bright orange double line, Caα (620.3–618.2mμ).

[1] Riesenfeld and Feld, *Z. anorg. allgem. Ch.*, **116**, 213–27 (1921). It is generally stated in the literature that the precipitate obtained with S^{--} is $Ca(OH)_2$. The work of these authors and experiments in this laboratory do not support this conclusion. Furthermore, a consideration of the molar solubility of the two compounds, $Ca(OH)_2$ and CaS, 0.0223 and 0.00294 respectively, and the fact that a precipitate can be obtained even from a solution of calcium sulfate (molar solubility 0.0121) lead one to expect the precipitate to be CaS rather than $Ca(OH)_2$.

[2] Hinds, *J. Am. Ch. Soc.*, **33**, 510–4 (1911), states that Ba^{++} and Sr^{++} are precipitated by SO_3^{--} in dilute acetic acid while Ca^{++} is not.

[3] Lambert and Schaffer, *J. Ch. Soc.*, **1926**, 2648–55, have studied the precipitation of $CaSO_4$.

[4] On the composition of the precipitate see: Smith, *J. Am. Ch. Soc.*, **42**, 259 (1920); Robinson, *J. Ag. Research*, **13**, 281 (1918), *C.A.* **13**, 1533; **12**, 1396.

[5] Wiley, *Ind. Eng. Ch., Anal. Ed.*, **3**, 127–9 (1931).

[6] See, however, Böttger, *Z. anal. Ch.*, **4**, 98 (1865). He states that the precipitate is soluble in excess of the reagent. Cf. Rüdisüle VI, 1, p. 767.

[7] Linck and Jung, *Z. anorg. allgem. Ch.*, **137**, 407–17 (1924), *C.A.* **18**, 3566.

[8] Decomposition starts above 600°.

8. Detection. — Calcium is precipitated as the carbonate along with Ba and Sr and separated from the former as described in §187, **8**. A portion of the solution of Sr^{++} and Ca^{++} is boiled with $(NH_4)_2SO_4$ (cf. 6, *e*). After standing some time — at least ten minutes — the filtrate is tested for Ca^{++}. Ammonium oxalate (cf. 6, *b*) gives a white precipitate, soluble in HCl.[1] The flame test should be applied to a portion of this solution to be sure that Ba and Sr are absent (cf. 5, *c* and 6, *b*).

9. Determination. — Calcium is usually precipitated as the oxalate, $CaC_2O_4 \cdot H_2O$, after removal of all metal ions except Mg^{++} and the alkalis.[2] This oxalate precipitate may be treated in several ways. (1) Ignition above 900° forms CaO which may be weighed. (2) Ignition at 450°–500° gives $CaCO_3 (CaC_2O_4 = CaCO_3 + CO)$ which may be weighed.[3] (This procedure has certain marked advantages over the first in that the product is stable in air whereas CaO must be carefully protected from moisture and CO_2.) (3) Solution in H_2SO_4 and titration of the oxalate ion with a suitable oxidizing agent $KMnO_4$ being the one most commonly employed.[4]

[1] Jackson, *J. Am. Ch. Soc.*, **25**, 992 (1903), states that ammonium oxalate is sensitive to Ca, 1 : 64,000; Sr^{++}, 1 : 32,000; Ba^{++}, 1 : 2000.

[2] It is interesting that in spite of the low solubility of MgC_2O_4 a quantitative separation can be effected. This probably is due to a marked difference in the rate of precipitation of the two salts under the existing conditions.

[3] Willard and Boldyreff, *J. Am. Ch. Soc.*, **52**, 1888–92 (1930).

[4] Cf. Rüdisüle, VI, 1, p. 775 *et seq.*; Hillebrand and Lundell, p. 493 *et seq.*

OUTLINE OF THE ANALYSIS OF GROUP V

(Starting with the filtrate from Group IV)

Metals, after removal of Groups I–IV, whose carbonates precipitate in ammoniacal solution with $(NH_4)_2CO_3$ in the presence of low concentration of NH_4Cl.

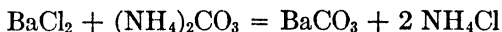
Metals	Ba	Sr	Ca
Ions in acid solution	Ba^{++}	Sr^{++}	Ca^{++}
Ions in NaOH solution	Ba^{++}	Sr^{++}	Ca^{++}
Ions in NH_4OH solution	Ba^{++}	Sr^{++}	Ca^{++}

Remove excess NH_4^+, make 0.25 *N* with NH_4Cl and *N* with NH_4OH		
Ba^{++}	Sr^{++}	Ca^{++}
	$(NH_4)_2CO_3$	
$BaCO_3$	$SrCO_3$	$CaCO_3$
	$HC_2H_3O_2$	
$Ba(C_2H_3O_2)_2$	$Sr(C_2H_3O_2)_2$	$Ca(C_2H_3O_2)_2$
	$K_2Cr_2O_7$	
$BaCrO_4$	$Sr(C_2H_3O_2)_2$	$Ca(C_3H_3O_2)_2$
HCl	Divide into 2 parts	
$BaCl_2$	0.1 *N* $(NH_4)_2SO_4$	*N* $(NH_4)_2SO_4$
H_2SO_4	$SrSO_4$	$SrSO_4$ $CaSO_4$
$BaSO_4$	flame test	$(NH_4)_2C_2O_4$
flame test		CaC_2O_4
		flame test

DIRECTIONS FOR THE PRECIPITATION AND ANALYSIS OF THE FIFTH GROUP

§191. In the directions given below it is assumed that Groups I–IV have been present and removed in the usual manner, the final filtrate being used for the precipitation of Group V. If one wishes to examine a solution directly for Group V, with Groups I–IV known to be absent, this may be done without any special preliminary operations. Start with the procedure which deals with the solution after any large excess of ammonium salts has been removed.

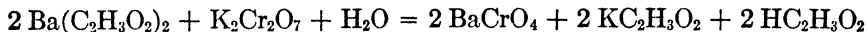
Manipulation.— Transfer the filtrate from Group IV (§138) to a casserole; evaporate carefully to dryness and heat the residue (at a hood), keeping the temperature below a red heat, until fumes of NH_4Cl are no longer given off. Cool, add a few drops of HCl, plus 15–20 cc. of H_2O, warm to dissolve the salts of Group V and VI metals, filter off and discard any slight residue of H_2SiO_3. To the filtrate add 2–3 cc. of NH_4Cl, plus 3–5 cc. excess of NH_4OH, heat nearly to boiling, and then add $(NH_4)_2CO_3$, 1–2 cc. at a time, until precipitation appears to be complete. Filter and test the filtrate with a little more $(NH_4)_2CO_3$ for completeness of precipitation. Barium, Sr and Ca form white precipitates of carbonates.

$$BaCl_2 + (NH_4)_2CO_3 = BaCO_3 + 2\,NH_4Cl$$

The filtrate is marked and set aside to test for Mg (§193) and Group VI (§211).

Dissolve the precipitate in 5–10 cc. of 2 *N* $HC_2H_3O_2$.

$$BaCO_3 + 2\,HC_2H_3O_2 = Ba(C_2H_3O_2)_2 + CO_2 + H_2O$$

Add 3–5 cc. of $NH_4C_2H_3O_2$ and 1–2 cc. of $K_2Cr_2O_7$. If Ba is present it will form a yellow precipitate.

$$2\,Ba(C_2H_3O_2)_2 + K_2Cr_2O_7 + H_2O = 2\,BaCrO_4 + 2\,KC_2H_3O_2 + 2\,HC_2H_3O_2$$

Add sufficient $K_2Cr_2O_7$ so that the solution is distinctly orange in color, shake, and let stand a few minutes for the $BaCrO_4$ to precipitate more completely, then filter and wash, setting aside the filtrate to test for Sr and Ca.

Dissolve the precipitate in HCl and add a few drops of H_2SO_4, obtaining a finely divided, white precipitate of $BaSO_4$. Filter, wash (rinsing the precipitate to the tip of the filter), moisten with 2–3 drops of HCl and apply the flame test. Barium gives an apple-green flame.

Divide the filtrate from $BaCrO_4$ into two parts, testing the first for Sr and the second for Ca.

(1) Add 5 cc. of 0.1 *N* $(NH_4)_2SO_4$, heat to boiling, then let stand about 5 minutes. A finely divided white precipitate indicates the presence of Sr. Filter, wash, moisten with a few drops of HCl, and apply the flame test. Strontium gives a rich crimson flame.

(2) If Sr is present, add to the second portion of the solution 5 cc. of *N* $(NH_4)_2SO_4$, boil for a few seconds, let stand 5 minutes, then filter and discard the precipitate. (The precipitate consists of $SrSO_4$ and some $CaSO_4$ if there is a moderate amount of Ca in the solution.) To the filtrate add 1–2 cc. of $(NH_4)_2C_2O_4$, boil and let stand a few minutes. A finely divided white precipitate indicates Ca. Filter, wash, moisten with a few drops of HCl, and apply the flame test. Calcium gives a brick red flame. If Sr is absent it is unnecessary to treat with $(NH_4)_2SO_4$ before adding $(NH_4)_2C_2O_4$.

§192. **Notes.** — 1. The filtrate from Group IV contains a large amount of ammonium salts, which must be removed if Group V metals are to be precipitated at all satisfactorily as carbonates. Barium, especially, fails to precipitate in the presence of high concentration of NH_4^+. Besides the method given above, two others are frequently used to remove NH_4^+. (*a*) The solution may be treated with 15–20 cc. of HNO_3 and evaporated carefully almost to dryness. As the solution becomes concentrated, molecular ammonium nitrate forms and decomposes.

$$NH_4NO_3 = N_2O + 2\,H_2O$$

(*b*) The solution may be treated with 3–4 g. of $NaHCO_3$, boiled until no more odor of NH_3 is evident, treated with a little more $NaHCO_3$ and odor noted. When sufficient $NaHCO_3$ has been used so that the final solution is alkaline and no odor of ammonia can be detected the ammonium salts are all removed.

$$NH_4Cl + NaHCO_3 = NaCl + NH_3 + CO_2 + H_2O$$

The evolution of CO_2 assists in removing the NH_3. In this procedure the Group V metals will precipitate as carbonates, along with more or less of $MgCO_3$. The precipitate may be filtered out (saving the filtrate to test for Mg and K) and dissolved in 10 cc. H_2O containing 1–2 cc. of 5 *N* HCl. Add 2 cc. NH_4Cl, 2–3 cc. excess of NH_4OH, and then precipitate with $(NH_4)_2CO_3$. Filter, combining the filtrate with the above filtrate to test for Mg, and analyzing the precipitate for Group V in the usual way.

2. A small amount of NH_4Cl is added to prevent the partial precipitation of Mg in Group V. The effect of NH_4^+ in controlling the concentration of CO_3^{--} supplied by $(NH_4)_2CO_3$ may be understood by noting that $(NH_4)_2CO_3$ is a salt derived from a weak base and a still weaker acid. It hydrolyzes largely to NH_4OH and HCO_3^-, the solution becoming slightly alkaline in the process. The addition of NH_4^+ lowers the concentration of OH^- in the solution, increasing the concentration of H^+ correspondingly. The latter combines with CO_3^{--}, lowering its concentration. In this way the concentration of CO_3^{--} may be kept low enough to prevent precipitation of $MgCO_3$ and still permit fair precipitation of the Group V carbonates. However, as stated in *Note* 1, if the concentration of NH_4^+ becomes very high it will lower the concentration of CO_3^{--} sufficiently to interfere with the precipitation of the Group V carbonates.

3. In testing for completeness of precipitation with $(NH_4)_2CO_3$, it must be remembered that small amounts of Group V metals do not precipitate readily. Therefore if one is concerned with identifying these metals in low concentrations it may be necessary to test the solution further after precipitation with $(NH_4)_2CO_3$ is complete. To do so, add 1–2 cc. each of $(NH_4)_2SO_4$ and $(NH_4)_2C_2O_4$ to the solution, boil, and let stand a few minutes, noting whether or not any precipitate forms. If it does, it may be prepared for analysis by filtering, washing, transferring to a beaker, and boiling for a few minutes with 15–20 cc. of 5 *N* Na_2CO_3. Any oxalate or sulfate is converted by this means to carbonate ($BaSO_4$ may require a second treatment with Na_2CO_3) which may be filtered out, washed, dissolved in acetic acid, and analyzed for Group V in the usual way.

4. If the solution is too acid, $BaCrO_4$ precipitates slowly and even incompletely. By using dilute $HC_2H_3O_2$ to dissolve the carbonates and by adding some $NH_4C_2H_3O_2$ to the solution these difficulties are decreased, but it is usually desirable to wait 2–3 minutes for satisfactory precipitation. Failure to precipitate Ba at this point will result in its appearing where Sr is expected.

5. In applying the flame test for Ba it is necessary to moisten the precipitate with HCl in order that a small amount of $BaCl_2$ may be formed. This compound may be volatilized in the flame while $BaSO_4$ is non-volatile at that temperature. The whole operation is best carried out as follows: After washing the precipitate to the tip of the filter, tear off this tip and spread it out, precipitate up, on a watch glass. Add two drops of 5 *N* HCl, then with a clean Pt wire (which does not of itself impart color to the Bunsen flame) scrape the precipitate back and forth a bit, then hold the wire in the outer edge of the Bunsen flame looking for the usual green color. The flame reaction in the case of Ba is less delicate than it would be if the salt dissolved more readily in the HCl, but with the manipulation just described it is possible to identify as little as 0.5 mg. of Ba. The Pt wire may be cleaned by dipping into HCl then holding in the flame for a moment, repeating this as often as necessary until it no longer colors the flame. This should be done immediately before trying the flame test on a precipitate.

6. The use of a Pt wire for the flame test is satisfactory only in cases where the salt volatilizes readily at the temperature of the Bunsen flame, and where a distinct color is obtained even with only an extremely minute amount of the vapor formed. Since the wire picks up less than 1 mg. of the solution it is only fair to the test to keep the volume of the solution very small. A confirmatory test can frequently be obtained by applying the flame test on a precipitate (after adding 2–3 drops of HCl) when the test on the original dilute solution is negative.

7. The separation of Sr from Ca is one of the least satisfactory of the ordinary procedures. Strontium sulfate is sufficiently insoluble so that 1 mg. of Sr in 10 cc. forms a visible precipitate on adding 5 cc. of 0.1 *N* $(NH_4)_2SO_4$ and boiling a short time. But with as little as 20 mg. of Ca^{++} present, precipitation fails with 2.5 mg. of Sr, while 100 mg. of Ca^{++} will prevent immediate precipitation of approximately 15 mg. of Sr. Many other metals besides Ca interfere with the precipitation of $SrSO_4$, but no explanation of this effect has been made. Several alternative separations have been worked out that are more accurate than the method used here, but they are sufficiently more time-consuming or difficult of operation so that it has seemed advisable to recommend the simpler rather than the more accurate method, calling attention at the same time to the difficulty of recognizing Sr in the presence of Ca. For a more accurate procedure one may use the chromate separation as worked out by Noyes (p. 116–7), with alcohol added to reduce the solubility of $SrCrO_4$ sufficiently to give satisfactory precipitation.

Another procedure that works fairly well, involves the removal of Ca before testing for Sr. To the solution containing Sr and Ca (after Ba has been precipitated with $K_2Cr_2O_7$) add NH_4OH and $(NH_4)_2CO_3$ to reprecipitate $SrCO_3$ and $CaCO_3$. Filter, wash, dissolve in dilute HCl, boil, and then neutralize with NH_4OH. Add 3–4 g. of solid NH_4Cl (solution should be practically saturated), then add 3–5 cc. of a freshly prepared 2 *N* $K_4Fe(CN)_6$ solution. Heat and let stand a few minutes, then test with a little more reagent for completeness of precipitation. The Ca forms a white precipitate whose composition is somewhat uncertain, being a triple ferrocyanide of K, Ca and NH_4. This removes Ca effectively if sufficient $K_4Fe(CN)_6$ is added. The filtrate may be tested for Sr as usual. Or, with Ca removed, the Sr may be precipitated with $(NH_4)_2C_2O_4$, since SrC_2O_4 precipitates more readily than $SrSO_4$ and dissolves more readily on moistening with HCl before applying the flame test.

8. If Ba is not removed completely as $BaCrO_4$ it will precipitate as $BaSO_4$ where Sr is expected. Therefore the flame test should be used to identify the Sr.

9. Strontium sulfate precipitates very slowly from a cold, dilute solution, but fairly readily at the boiling point, so it is necessary to heat the solution after adding the dilute $(NH_4)_2SO_4$ before judging concerning the presence or absence of Sr. Further, the amount of SO_4^{--} introduced at this point is kept small intentionally (to avoid precipitation of $CaSO_4$), so the quantity of $SrSO_4$ precipitated at best is rather limited. However, even though the precipitate is slight in amount, the confirmatory flame test will be entirely satisfactory if the manipulation is carried out with reasonable care as described above (*Note* 5).

10. It is necessary to remove Sr before testing for Ca, otherwise SrC_2O_4 would precipitate and interfere with the identification of Ca. The Sr is removed by precipitating as $SrSO_4$ with excess of $(NH_4)_2SO_4$, boiling and letting stand several minutes for completeness of precipitation. In this process a more concentrated reagent is used than in testing for the presence of Sr, so part of the Ca is usually removed at the same time. But $CaSO_4$ is sufficiently soluble even in the presence of excess of $(NH_4)_2SO_4$ so that enough Ca will be left in solution to permit satisfactory identification.

11. The flame tests for Sr and Ca are much less distinctive when tried on side table solutions than with the precipitates obtained in the course of analysis in Group V. This is due to the presence of Na^+ in the former solutions, from slight action of these solutions on the glass bottles. To obtain the more characteristic flames the Sr or Ca may be precipitated from the side table solutions as $SrSO_4$, or CaC_2O_4, this filtered out and washed thoroughly, then the flame test applied as in the regular analysis. Under such conditions (especially when viewed against a dark background) the two flames are easily distinguished from each other.

12. In the tests for Sr and Ca a small, direct vision, hand spectroscope is very useful. Strontium and Ca each show two characteristic bands of color which are easily seen by viewing the flame tests through this instrument. Thus Sr shows bands in the deep red and bright orange, while Ca shows bands in the bright red and green. By examining known substances first, it becomes easy to identify Sr and Ca either separately or in the presence of each other.

13. Group V metals are frequently lost in appreciable quantities in earlier group precipitations. Thus the moist sulfides in Groups II and IV may absorb oxygen from the air and undergo oxidation to sulfate sufficiently to remove small amounts of Ba in these groups. Also, when boiling out H_2S in the filtrate from Group II, more or less of the H_2S may be oxidized by HNO_3 in the solution with corresponding precipitation of $BaSO_4$ or $SrSO_4$. Such a precipitate may be filtered out, boiled with concentrated Na_2CO_3 to convert to carbonates, then filtered, washed and tested as in Group V for Ba and Sr. Finally, all three of the metals may be lost to some extent by precipitation as carbonates in Groups III and IV, due to CO_3^{--} in the NH_4OH used, and to further absorption of CO_2 from the air by the alkaline solution. These errors may be exaggerated by letting the solutions stand unnecessarily while analyzing intervening group precipitates. Greater accuracy may be obtained in Group V by starting with a fresh portion of the original solution, precipitating Groups I and II rapidly and discarding these precipitates, then precipitating Groups III and IV with H_2S in the presence of NH_4OH, filtering, and using the filtrate immediately for Group V.

14. Alternative procedures for the separation of Ba, Sr and Ca from each other are occasionally recommended. Thus Noyes has worked out a careful set of directions for the precipitation of Ba as $BaCrO_4$ in an acetic acid-sodium acetate solution, followed by precipitation of Sr as $SrCrO_4$ in an alkaline solution with excess K_2CrO_4, using alcohol to reduce the solubility of the $SrCrO_4$. Calcium is identified in the final filtrate.

Another scheme that has been widely used depends upon the differences in solubility of some of the dry salts of Ba, Sr and Ca in alcohol. Dissolve the Group V precipitate in HCl, evaporate to dryness on the water bath, powder the residue, and digest it for a short time with absolute alcohol. The $BaCl_2$ remains as a residue, but the $SrCl_2$ and $CaCl_2$ dissolve. Filter and wash with alcohol. Dissolve the residue in water and apply the usual tests for Ba. Evaporate the filtrate to dryness to remove the alcohol, add HNO_3 and evaporate to dryness to convert the chlorides to nitrates, then digest again with alcohol. The $Ca(NO_3)_2$ dissolves, leaving $Sr(NO_3)_2$ as a precipitate. Dissolve the latter in water and test as usual for Sr. The $Ca(NO_3)_2$ solution is evaporated to dryness to remove the alcohol, the residue being dissolved in water for the confirmatory tests for Ca.

§193. Magnesium (*Magnesia*, a district in Thessaly). Mg = 24.32. Atomic No. 12. Valence 2. Isolated by Bussy in 1829.

1. Physical Properties. — Density, 1.75;[1] melting point, 651°;[2] boiling point, 1380° ± 5°.[3] Magnesium is a silvery white metal, malleable and ductile at higher temperatures, slightly harder than Sn. It is not acted upon appreciably by H_2O or alkalis at room temperature, and only slightly at 100°. When heated in air or oxygen it burns with incandescence to MgO. Curiously enough the kindling point (*ca.* 800°) is much higher than the melting point; hence castings can be made without serious difficulty. It combines directly when heated with N, P, As, S and Cl. Magnesium is extensively used in photographic flashlight powders, in signal flares, as a " getter " in radio tubes, a deoxidizer in bronze, monel metal and other castings. Aluminum alloys containing a small amount of Mg are extensively used in aeroplane construction because of their high tensile strength per unit weight.

2. Occurrence. — Magnesium is a major constituent of the earth's crust (2.24%) being eighth among the elements in order of abundance.[4] It does not occur native. The more important ores are magnesite, $MgCO_3$, dolomite, $MgCa(CO_3)_2$, and brucite, $Mg(OH)_2$ (an alteration product of serpentine, $H_2Mg_3Si_4O_{12}$). Practically all hard waters contain some Mg^{++}. Commercially, probably the most important of the ores is magnesite. In 1928 the total world production of this material was well over 800,000 metric tons of which Austria produced a little less than one-half. The United States (California and Washington), Greece and Russia together mined an equal amount.[5] In the past the major demand for Mg involved use of the calcined ore as a heat insulator, refractory, cement (Sorel), adulterant of paint, etc. Epsom salts ($MgSO_4 \cdot 7H_2O$) was made to the extent of about 90,000,000 lbs. in 1929. The demand for metallic magnesium has increased rapidly during recent years amounting to over a million pounds in the year last mentioned.[6] The price of ingot magnesium is about 75¢ per pound.

3. Preparation. — In the United States practically all of the metallic magnesium is made by electrolyzing fused, anhydrous magnesium chloride obtained as a by-product from certain bittern waters at Midland, Michigan.[7]

4. Oxide and Hydroxide. — Only one oxide, MgO, is known with certainty. It is formed by burning the metal in air, and by the action of heat upon the hydroxide, carbonate, nitrate, sulfate, oxalate, etc. The hydroxide, $Mg(OH)_2$, is formed by treating Mg^{++} with a fixed alkali.

5. Solubilities. — *a. Metal.* — Magnesium is soluble in acids, including carbonic, evolving hydrogen: $Mg + CO_2 + H_2O = MgCO_3 + H_2$, $MgCO_3 + CO_2 + H_2O = Mg(HCO_3)_2$. It is also attacked by alkali bicarbonates, as $NaHCO_3$, and various salts having an acid reaction.[8]

b. Oxide and Hydroxide. — In contact with water MgO is very slowly changed to the hydroxide and absorbs CO_2 from the air. It is readily soluble in acids. Magnesium hydroxide, $Mg(OH)_2$, is insoluble in water;[9] soluble in acids and ammonium salts.[10]

[1] Biltz and Pieper, *Z. anorg. allgem. Ch.*, **134**, 23 (1924).

[2] B. Stds. Cir. 35.

[3] Hartmann and Schneider, *Z. anorg. allgem. Ch.*, **180**, 275–83 (1929), *C.A.* **23**, 4383.

[4] U. S. Geol. Survey Bull. 770, **1924**, p. 29.

[5] Mineral Ind., **1929**, p. 412–23.

[6] In Europe Mg is used more extensively than in the United States. The I. G. Farbenindustrie alone produces annually about 4 million pounds for its "elektron" alloys.

[7] Cf. Billiter, Technische Elektrochemie, Wilhelm Knapp, Halle, Vol. III, 2nd. ed., **1932**, p. 83.

[8] Tarlé, *Bull. Ch. Soc. Japan*, **5**, 57–64 (1930), *C.A.* **24**, 3421.

[9] Travers and Nouvel, *Compt. rend.*, **188**, 499–501 (1929), *C.A.* **23**, 2632.

[10] Due to a lowering of the $[OH^-]$.

c. Salts. — The chloride, bromide, iodide, chlorate, nitrate and acetate are deliquescent, the sulfate (7 H_2O) slightly efflorescent. The carbonate, phosphate ($MgNH_4PO_4 \cdot 6H_2O$ — 0.04 g./100 cc. at 20°; $MgHPO_4 \cdot 3H_2O$ — 0.3 g./100 cc. at room temperature), borate, arsenite, arsenate (0.04 g./100 cc. at 20°), fluoride, oxalate (0.03 g./100 cc. solution at 18°) are insoluble in H_2O. The sulfite, phosphite and tartrate are slightly soluble in H_2O. The carbonate is soluble, the phosphate, arsenite and arsenate are insoluble in solutions of ammonium salts.

6. Reactions. — *a.* The fixed alkali and other alkaline earth hydroxides precipitate Mg^{++} as $Mg(OH)_2$, white, gelatinous. It is insoluble in excess of the reagent. No precipitation takes place in the presence of ammonium salts (cf. 5, *b*). With NH_4OH alone a part of the Mg^{++} ions are precipitated as $Mg(OH)_2$: $MgCl_2 + 2 NH_4OH \rightleftarrows Mg(OH)_2 + 2 NH_4Cl$. If sufficient NH_4^+ is present initially no precipitate is obtained. The fixed alkali carbonates precipitate basic magnesium carbonate, $4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$, composition somewhat variable depending upon conditions.[1] Ammonium carbonate[2] does not precipitate Mg^{++} in the presence of other highly ionized ammonium salts. Bicarbonates of the alkalis do not precipitate Mg^{++} in the cold; upon boiling, CO_2 is evolved and the carbonate is precipitated ($MgCO_3 \cdot 3H_2O$).[3]

b. In spite of the fact that magnesium oxalate is classed among the insoluble salts, if $C_2O_4^{--}$ is added to a solution containing Mg^{++}, either acid or ammoniacal, no precipitate is obtained even upon standing for some time. Two possible explanations[4] involve (1) formation of a complex ion and (2) supersaturation. If an equal volume of glacial acetic acid, ethyl alcohol or acetone is added the Mg^{++} quickly precipitates.

Potassium ferrocyanide added to a cold solution of Mg^{++} gives a white, crystalline precipitate of $MgK_2Fe(CN)_6$. If NH_4^+ is present the product will be a triple salt. The rate of separation in either case will depend largely on the concentration of Mg^{++}.

Potassium ferrocyanide or ferricyanide added to a solution of Mg^{++} containing Rb^+ or Cs^+ gives a white precipitate. The test is improved by the addition of alcohol.[5] This is said to be one of the most delicate tests known for Mg.[6]

d. Alkali phosphates, as Na_2HPO_4, precipitate Mg^{++} as $MgHPO_4$ from

[1] Cf. Nishimura, *Bull. Inst. Phys. Ch. Research* (*Tokyo*) English ed., **1**, 77–80 (1928), *C.A.* **23**, 50.

[2] Cf. Fichter and Osterwalder, *Z. anal. Ch.*, **55**, 389–92 (1916), *C.A.* **11**, 1612.

A concentrated solution of $(NH_4)_2CO_3$ will precipitate Mg^{++} fairly completely from a solution containing 30%–40% alcohol.

[3] Nanty, *Compt. rend.*, **152**, 605–7 (1910), *C.A.* **5**, 1885.

[4] Cf. Astruc and Camo, *J. pharm. ch.*, **17**, 381–6 (1918), *C.A.* **12**, 2481.

[5] Murmann, *Oesterr. Ch. Ztg.*, **28**, 42–4 (1925), *C.A.* **19**, 1827.

[6] Cf. Feigl and Pavelka, *Mikrochemie*, **2**, 85–91 (1924), who use $(NH_4)_4Fe(CN)_6$ and claim a delicacy greater than that of the phosphate test.

neutral solution,[1, 2] $MgNH_4PO_4$ from ammoniacal solution by addition of NH_4OH to a solution containing Mg^{++} and PO_4^{-3}. If the phosphate is added to an ammoniacal solution of Mg^{++}, $Mg_3(PO_4)_2$ is precipitated. In the case of $MgNH_4PO_4$, which is crystalline, there is a tendency to supersaturation which usually may be overcome by rubbing the test tube or beaker beneath the surface of the liquid with a stirring rod. The presence of an ammonium salt prevents the precipitation of any $Mg(OH)_2$. The precipitate is readily soluble in acetic or oxalic acid as well as the mineral acids.

e. Magnesium sulfide is decomposed by H_2O, and Mg^{++} is not precipitated by H_2S or $(NH_4)_2S$. The addition of Na_2S results in a separation of $Mg(OH)_2$. Soluble sulfates do not precipitate Mg^{++} (distinction from Ba^{++}, Sr^{++} and Ca^{++}). The anhydrous sulfate, however, is insoluble in H_2O and dilute acids.

g. Soluble arsenates precipitate Mg^{++} as do the corresponding phosphates.

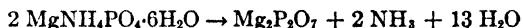
7. **Ignition.** — If $MgNH_4PO_4$ is heated it loses H_2O and NH_3, becoming magnesium pyrophosphate, $Mg_2P_2O_7$. Ignition of the carbonate gives MgO. In dry air $MgCl_2$ may be ignited without decomposition, but in the presence of moisture MgO and HCl are formed.

8. **Detection.** — *a.* After the removal of all metals belonging to previous groups, Mg^{++} may be detected by adding $(NH_4)_2HPO_4$ to the cold acid solution and then making it alkaline with dilute NH_4OH, stirring vigorously during the neutralization. The precipitate must be crystalline.

b. A number of organic reagents have been suggested for the detection of Mg^{++}. The majority of them depend upon the formation of a blue color. Mg^{++} treated with a hot, alkaline, alcoholic solution of diphenylcarbazide gives a bluish-violet color.[3] An alkaline solution of 1, 2, 5, 8, tetrahydroxyanthraquinone changes in color from blue violet to a cornflower blue in the presence of 0.001 mg. Mg^{++} per cc. Aluminum interferes in the absence of tartrate, and phosphate decreases the sensitivity of the test.[4] If Mg^{++} is treated with *o-p*-dihydroxyazo-*p*-nitrobenzene a blue color will develop when 0.002 mg. or more of Mg is present.[5] When an alkaline solution of titan yellow is added to Mg^{++} a red color develops. It is intensified by Ca and Ba while Al, Sn and Bi interfere.[6, 7]

[1] If the solution is boiled the precipitate is $Mg_3(PO_4)_2 \cdot 7H_2O$.
[2] Cf. Balarew, *Z. anorg. allgem. Ch.*, **102**, 241–6 (1918), *C.A.* **12**, 2288.
[3] Feigl, *Z. anal. Ch.*, **72**, 113–9 (1927), *C.A.* **22**, 41.
[4] Hahn, *et al.*, *Ber.*, **57B**, 1394–6 (1924), *C.A.* **19**, 797.
[5] Ruigh, *J. Am. Ch. Soc.*, **51**, 1456–7 (1929).
[6] Kolthoff, *Ch. Weekblad*, **24**, 254 (1927).
[7] For other tests see Eegriwe, *Z. anal. Ch.*, **76**, 354–9 (1929), *C.A.* **23**, 2903.

9. Determination. — Magnesium is usually precipitated as $MgNH_4PO_4 \cdot 6H_2O$, ignited to $Mg_2P_2O_7$ and weighed as such.[1]

$$2\ MgNH_4PO_4 \cdot 6H_2O \rightarrow Mg_2P_2O_7 + 2\ NH_3 + 13\ H_2O$$

Precipitation with 8-hydroxyquinoline (8-Quinolinol) as $Mg(C_9H_6ON)_2$, drying at 130°–140° and weighing has been found satisfactory in certain cases.[2]

Volumetrically, magnesium may be determined by solution of the dried $MgNH_4PO_4$ precipitate in excess of standardized H_2SO_4 and titration of the excess with NaOH using methyl orange as indicator.[3]

10. Oxidation and Reduction. — Magnesium is a powerful reducing agent. When it is ignited with the oxides or carbonates of the following elements MgO is formed and the corresponding element is liberated: Ag, Hg, Pt, Sn, B, Al, Th, C, Si, Pb, P, As, Sb, Bi, Cr, Mo, Mn, Fe, Co, Ni, Cu, Cd, Zn, Be, Ba, Sr, Ca, Rb, K, Na and Li. In some cases the reaction takes place with explosive violence. From their corresponding salts in neutral solution Mg° precipitates Se, Te, As, Sb, Bi, Sn, Zn, Cd, Pb, Tl, Th, Cu, Ag, Mn, Fe, Co, Ni, Au, Pt and Pd.

THE ALKALI GROUP AND MAGNESIUM (SIXTH GROUP)

(MAGNESIUM) **POTASSIUM, SODIUM, AMMONIUM**
CESIUM, RUBIDIUM, LITHIUM

§205. Potassium (English *pot ash*) (Kalium). K = 39.10. Atomic No. 19. Valence 1. Isolated by Davy, 1807.

1. Physical Properties. — Density, 0.8621;[4] melting point, 62.3°;[5] boiling point, 760°. Potassium is a silvery white metal with a bluish tinge. At room temperature it is of a wax-like consistency, ductile and malleable; at 0° it is brittle. It is harder than Na, softer than Li, Pb, Ca and Sr. The glowing vapor is a beautiful intense violet. Next to Cs and Rb it is the most electro-positive of all metals,[6] remains unchanged in dry air, oxidizes rapidly in moist air, and decomposes H_2O with great violence, evolving H_2 and burning with a violet flame. Potassium is usually kept under kerosene. Metallic potassium has no extensive commercial uses; the chloride and sulfate are important as fertilizer ingredients for agricultural purposes.

[1] Hoffman and Lundell, *B. Stds. J. Research*, **5**, 286–93 (1930).
[2] Hillebrand and Lundell, p. 114–7; Berg, *Z. anal. Ch.*, **71**, 23–36 (1927), *C.A.* **21**, 2449.
[3] Handy, *J. Am. Ch. Soc.*, **22**, 31 (1900).
[4] Richards and Brink, *J. Am. Ch. Soc.*, **29**, 117–27 (1907).
[5] B. Stds. Cir. 35.
[6] No. 87 is not considered.

2. Occurrence. — Potassium is very widely distributed as a constituent of igneous rocks, etc. It exists in the lithosphere of the earth to the extent of about 2.58%. For many years the most important commercial source has been the Stassfurt deposits of carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$; kainite, $K_2Mg(SO_4)_2 \cdot MgCl_2 \cdot 6H_2O$; etc. More recently extensive veins of potash salts have been found in southwestern United States. The Searles Lake deposit may also soon become a factor in the situation. The world production, calculated on a K_2O basis, now approximates 2,000,000 metric tons, of which Germany produces 69%, France 22%, the United States, Poland and Spain together about 7%.

3. Preparation. — Electrolysis of fused KOH in a specially constructed cell is probably the only method used.[1]

4. Oxides and Hydroxide. — Potassium oxide, K_2O, may be prepared by carefully heating the metal with the necessary amount of oxygen (air). It is a hard, gray mass, melting above a red heat. Water changes it to KOH with the generation of much heat.[2] Potassium hydroxide, KOH, is obtained by boiling a solution of K_2CO_3 with BaO, SrO or CaO. The most important commercial method, however, is electrolysis of the chloride. Pure, water-free KOH is a white, hard, brittle mass, melting at about 360°. It dissolves in H_2O with the liberation of much heat. Potassium peroxide, K_2O_4,[3] is formed when the metal is heated with an excess of oxygen. It is an amorphous powder about the color of $PbCrO_4$, decomposed by moist air or H_2O with evolution of O_2. It is a powerful oxidizing agent, changing S° to S^{+6}, P° to P^{+5}, K, As, Sn, Sb, Zn, Cu, Fe, Ag and Pt to the oxides.

5. Solubilities. — The metal and its oxides dissolve in H_2O with violent action, forming KOH. Potassium dissolves in alcohol, forming potassium alcoholate, C_2H_5OK, and H_2. Potassium chloroplatinate, acid tartrate, fluosilicate, picrate, phosphomolybdate, perchlorate, cobaltinitrite, periodate, fluotitanate, fluozirconate and zirconium sulfate are slightly soluble to insoluble in cold water and practically insoluble in alcohol. The carbonate and sulfate are insoluble in alcohol.

6. Reactions. — *a.* Potassium and sodium hydroxides are very strong bases, and precipitate from solution ions of all the other metals (except As, Tl^+, Cs, Li and Rb), as oxides or hydroxides. These precipitates are quite insoluble in H_2O (except $Ba(OH)_2$, $Sr(OH)_2$ and $Ca(OH)_2$). Excess of the reagent causes the Pb, Sb, Sn, Al, Cr and Zn precipitates to dissolve[4] (i.e., the hydroxides of these metals are amphoteric) forming K_2PbO_2, $KSbO_2$, Na_2SnO_2, etc. Potassium carbonate precipitates positive metal ions, except Cs, Rb, Na and Li. The normal carbonate is formed with Ag^+, Hg^{++}, Cd^{++}, Fe^{++}, Mn^{++}, Ba^{++}, Sr^{++}, Ca^{++} and Mg^{++}; the oxide with Sb^{+3}; the hydrated oxide with Sb^{+5} and Sn^{+4}; the hydroxide with Sn^{++}, Fe^{+3}, Al^{+3}, Cr^{+3} and Co^{+3}; a basic salt with Hg^{++} and a basic carbonate with the other metals.[5]

b. Tartaric acid, $H_2C_4H_4O_6$, or more readily sodium bitartrate, $NaHC_4H_4O_6$, precipitates, from solutions sufficiently concentrated, potassium bitartrate, $KHC_4H_4O_6$, clear, crystalline. If the solution is initially alkaline it should be acidified with tartaric acid. Only ions of the alkali

[1] Cf. Hackspill, *Ann. ch. phys.*, [8] **28**, 613 (1913).

[2] Rengade, *Compt. rend.*, **143**, 1152 (1906).

[3] Cf. Riesenfeld and Mau, *Ber.*, **44**, 3595 (1911).

[4] Colloid chemists have suggested that peptization takes place, that the hydroxide is merely dispersed in the solvent and that a true solution is not formed.

[5] Ag_2CO_3 and Hg_2CO_3 decompose, quickly upon heating, to form Ag_2O and $HgO + Hg$ respectively.

metals may be present. Precipitation is increased by agitation and by addition of alcohol. The precipitate is soluble in H_2O to the extent of 0.57 g./100 cc. at 20°, in mineral acids, and in alkaline solution forming the more soluble normal salt, $K_2C_4H_4O_6$. It is insoluble in 50% alcohol.[1]

c. A solution of sodium cobaltinitrite gives, in solutions of K^+ acidified with acetic acid, a golden yellow precipitate[2] of $K_2NaCo(NO_2)_6 \cdot H_2O$.[3] In concentrated solutions the precipitate forms immediately. Dilute solutions should be allowed to stand for some time, although warming will hasten the separation. Since NH_4^+ gives a similar precipitate, it must be completely removed. Iodides and other reducing agents must also be absent. Many modifications of this test to increase its delicacy have been suggested, among them being the addition of other ions as Ag^+, Pb^{++}, Hg_2^{++}, etc.,[4] the presence of which make it possible to detect less than one part of potassium in 10,000 of solution.

e. If to an alcoholic solution of sodium bismuth thiosulfate, $Na_3Bi(S_2O_3)_3$, is added a solution of K^+, a yellow precipitate of the corresponding potassium salt is obtained. The test is very delicate, depending in this respect, however, on the amount of alcohol present. Apparently NH_4^+, Ba^{++} and Sr^{++} interfere. The reagent is unstable.[5]

f. Fluosilicic acid, H_2SiF_6, added in excess to a neutral solution containing K^+, gives a gelatinous precipitate of the potassium salt, K_2SiF_6. If the solution is alkaline silicic acid separates, which is easily mistaken for the salt.[6]

Chloroplatinic acid, H_2PtCl_6, forms in concentrated, acid solutions of K^+, a crystalline yellow precipitate of potassium chloroplatinate, K_2PtCl_6. Although slightly soluble in H_2O, it is practically insoluble in 80% alcohol. A solution of NH_4^+ also gives the test. The presence of I^- or CN^- inhibits the reaction. In either case evaporation of the sample with concentrated HCl will eliminate the difficulty. Large amounts of Na^+ decrease the delicacy of the test.

A solution of perchloric acid, $HClO_4$, forms with K^+ a crystalline, white precipitate of potassium perchlorate, $KClO_4$, almost insoluble in absolute alcohol containing 0.2% $HClO_4$. The ammonium salt is only slightly

[1] Winkler, *Pharm. J.*, **94**, 741 (1915), *C.A.* **9**, 2012. For the preparation of "a good tartaric acid reagent" see Ajon, *Rivisti ital. essenze profumi*, **11**, 6–7 (1929), *C.A.* **23**, 1588.

[2] de Koninck, *Z. anal. Ch.*, **49**, 53 (1910).

[3] Wassiliev and Matwejev, *Z. anal. Ch.*, **81**, 106–14 (1930), *C.A.* **24**, 4730; Bonneau, *Bull. soc. ch.*, **45**, 798–808 (1929), *C.A.* **24**, 800. In concentrated solution $K_3Co(NO_2)_6$ is formed.

[4] Burgess and Kamm, *J. Am. Ch. Soc.*, **34**, 652–9 (1912).

[5] Pauly, *Z. anal. Ch.*, **36**, 512 (1897); cf. Lutz, *Ibid.*, **59**, 145 (1920), *C.A.* **14**, 2770.

[6] Stolba, *J. prakt. Ch.*, **103**, 396 (1868).

soluble in this medium. All other metals are readily soluble except Cs and Rb.[1]

g. Many other slightly soluble potassium salts have been studied and recommended for use in analytical chemistry. Among the reagents are phosphotungstic acid,[2] phosphomolybdic acid,[3] sodium chromate with uranyl nitrate,[4] and picric acid.[5]

7. Ignition. — Potassium compounds color the flame violet. The presence of a very small quantity of sodium enables its yellow flame to completely obscure the violet of potassium. Owing to the greater volatility of the latter, flashes of violet are sometimes seen on the first introduction of the wire even when enough Na is present to conceal the violet at full heat. Looking at the flame through a "cobalt glass" of the proper color and thickness[6] will make it appear red, because the yellow rays are absorbed. With dilute solutions of K^+ there may be only a flash of color. If organic substances are present, they must be removed by ignition below a red heat.

The volatile potassium compounds, when placed in the flame, give two characteristic lines, the red $K\alpha$ (769.9mμ) and the indigo blue $K\beta$ (404.4mμ).

8. Detection. — *a.* Potassium is usually identified by the violet blue color that most of its salts impart to the Bunsen flame (cf. 7). Some of the heavy metals interfere; hence, the test should be made after their removal (§213–4).

Potassium may be precipitated as the cobaltinitrite, chloroplatinate, perchlorate, fluosilicate, bitartrate, etc. Most of these reactions are used for the quantitative precipitation of K under carefully controlled conditions; they are seldom used for its detection.

b. Organic reagents suggested for the detection of K include picric acid[7] (or sodium picrate), and lokaonic acid,[8] 6-chloro-5-nitro-*m*-toluene sodium sulfonate.[9]

9. Determination. — *Gravimetrically,* potassium may be precipitated as (1) K_2PtCl_6, dried at 130° and weighed as such; (2) $KClO_4$, dried first at 110°, then for 15 minutes at 350°, and weighed as such;[10] (3) $NaK_2Co(NO_2)_6 \cdot H_2O$, dried at 110°, and weighed as

[1] Thin and Cumming, *J. Ch. Soc.*, **107**, 361 (1915); cf. Smith, G. F., *J. Am. Ch. Soc.*, **45**, 2072–80 (1923), who recommends butyl alcohol containing 0.5%–1% $HClO_4$.

[2] Meyer, *Ch. Ztg.*, **31**, 158–9 (1907).

[3] Schlicht, *Ibid.*, **30**, 1299 (1906).

[4] Gaspar y Arnal, *Chimie & industrie*, **20**, 631–2 (1928), *C.A.* **23**, 576.

[5] See Caley, *J. Am. Ch. Soc.*, **52**, 953–6 (1930).

[6] Satisfactory "glasses" may be made by thoroughly "fixing" and washing unexposed lantern slides and staining the film with a 1% solution of crystal violet. After drying, the film may be protected by a cover glass and bound with adhesive tape, or preferably, mounted in a wooden frame. Meyer, *Helv. Ch. Acta*, **8**, 146–8 (1925), *C.A.* **19**, 1984. A solution of chrome alum (310 g./l.) 3 cm. thick also makes a good filter. McCay, *J. Am. Ch. Soc.*, **45**, 2958 (1923).

[7] Minovici and Ionescu, *Bull. soc. ch. România*, **3**, 25–33 (1921), *C.A.* **15**, 3045.

[8] Cf. Gutzeit, *Helv. Ch. Acta*, **12**, 713–40 (1929), *C.A.* **23**, 4644; and especially for delicacy: Lutz, *Z. anal. Ch.*, **59**, 145 (1920).

[9] Davies and Davies, *J. Ch. Soc.*, **123**, 2976–82 (1923), *C.A.* **18**, 383.

[10] Smith and Ross, *J. Am. Ch. Soc.*, **47**, 774, 1020 (1925). Smith, G. F., *Ibid.*, p. 762; Willard and Smith, *Ibid.*, **45**, 293 (1923); **44**, 2816 (1922).

such.[1] *Volumetrically,* the cobaltinitrite precipitate may be treated with an excess of $KMnO_4$ and the excess determined with oxalic acid.[2]

10. Oxidation and Reduction. — Potassium is a very powerful reducing agent; its affinity for oxygen, at temperatures not too high, is greater than that of any other element except Cs and Rb. (For the oxidizing action of K_2O_4 see 4.)

§206. Sodium (English *soda*) (Natrium) Na = 22.997. Atomic No. 11. Valence 1. Isolated by Davy, 1807.

1. Physical Properties. — Density, 0.97;[3] melting point, 97.5°;[4] boiling point, 882.90°.[5] Sodium is a silvery white metal with a strong metallic luster. At room temperature it is softer than Pb and can be pressed together between the fingers (caution!); at −20° it is quite hard, at 0° very ductile. It is a good conductor of heat and electricity, standing next to Ag, Cu and Au as regards the latter property. It oxidizes rapidly in moist air, hence must be kept under benzene or kerosene. It decomposes water violently, even at room temperature, evolving H_2, which frequently ignites; $2\ Na + 2\ H_2O = 2\ NaOH + H_2$. It burns at a red heat with a yellow flame. Pure, dry Na is not attacked by dry HCl.[6] Commercially there is very little demand for Na.

2. Occurrence. — Sodium does not occur native, but in its various combinations comprises 2.75% of the lithosphere. The ocean contains about 3% NaCl. It is found in enormous deposits as rock salt, NaCl; as Chile saltpeter, $NaNO_3$; in lesser quantities as the borate, carbonate, sulfate, etc. The production of salt, NaCl, in the United States amounted to about 54,000,000 barrels (280 lbs. each) in 1928. Michigan and New York together contributed over half of this quantity. During the same year Chile produced over 3,000,000 tons of saltpeter.

3. Preparation. — The electrolysis of fused sodium hydroxide is the only method of any importance.

4. Oxides and Hydroxide. — Sodium oxide, Na_2O, is formed by burning Na° in oxygen or in air and heating again with Na° to decompose the Na_2O_2. The monoxide is white when cold and very hygroscopic. Heated above 400° it forms Na° and Na_2O_2. Sodium hydroxide, NaOH, is formed by dissolving the metal or oxide in water; by treating a solution of Na_2CO_3 with BaO, SrO, or CaO; by electrolysis of NaCl (the commercially important process). It is a white, opaque, brittle, crystalline compound, melting at 318.4°[7] and volatilizing without decomposition at a somewhat higher temperature. It is very hygroscopic.

Sodium peroxide, Na_2O_2, is made by heating Na° in an iron tube at 300° in the presence of dry, CO_2-free air. The product has a purity of about 93%, is yellowish in color and may be fused without decomposition. It dissolves in water to form the system, $Na_2O_2 + 2\ H_2O \rightleftarrows 2\ NaOH + H_2O_2$. It reacts as H_2O_2, i.e., either as an oxidizing or reducing agent, depending upon conditions.

5. Solubilities. — Sodium and sodium oxide dissolve in water, forming the hydroxide (51.7 g. of $NaOH{\cdot}H_2O$ dissolve to make 100 g. of solution at 25°). In acid the corresponding sodium salts are formed, all soluble in H_2O except sodium pyroantimonate and

[1] Le Boucher, *Anales soc. españ. fís. quím.*, **23**, 540–58 (1925), *C.A.* **20**, 1366.
[2] Bowser, *J. Am. Ch. Soc.*, **33**, 1752–7 (1911).
[3] Richards and Brink, *J. Am. Ch. Soc.*, **29**, 117 (1907).
[4] B. Stds. Cir. 35; cf. Bidwell, *Phys. Rev.*, [2] **23**, 368 (1924).
[5] Heycock and Lamplough, *J. Ch. Soc.* (*Proc.*), **28**, 3 (1912).
[6] Cf. Gmelin, 8th ed. No. 21, p. 139 *et seq.*
[7] Hevesy, *Z. physik. Ch.*, **73**, 667 (1910).

fluosilicate, which are only slightly soluble. The nitrate and chlorate are deliquescent The carbonate (10 H_2O), sulfate (10 H_2O), sulfite (8 H_2O), phosphate (12 H_2O), and the acetate (3 H_2O) are efflorescent.

6. **Reactions.** — *a.* As reagents NaOH and Na_2CO_3 react like the corresponding potassium salts (§205, 6, *a*).

b. Solutions of soluble oxalates precipitate, from a sufficiently concentrated solution of Na^+, crystalline, white sodium oxalate, soluble in mineral acids, in H_2O to the extent of 3.1 g./100 g. of solution at 15°.[1] Precipitation does not take place from a solution of $Na_2B_4O_7$.

Various triple acetates of Na have been studied and found relatively insoluble compounds. Zinc uranyl acetate gives with neutral, fairly concentrated, solutions of Na^+ a yellow, crystalline precipitate of $NaZn(UO_2)_3(C_2H_3O_2)_9{\cdot}6H_2O$.[2] Corresponding Mg[3] and Co[4] salts are similar in appearance and properties.

f. A solution of H_2SiF_6 will precipitate sodium fluosilicate from a sufficiently concentrated solution of Na^+. (The solubility of Na_2SiF_6 is 0.65 g./100 g. of solution at 17.5°. In an alcoholic solution the value is much lower.)[5]

A solution of chloroplatinic acid, H_2PtCl_6, gives a precipitate of sodium chloroplatinate only from a concentrated solution. The crystals are readily distinguished from those of the potassium or ammonium salt in that they are red.

g. A solution of potassium pyroantimonate, $K_2H_2Sb_2O_7$, produces in neutral or alkaline solutions of Na^+ a slow-forming, white, crystalline precipitate, $Na_2H_2Sb_2O_7{\cdot}6H_2O$, slightly soluble in cold H_2O. Precipitation can often be accelerated by rubbing the test tube, under the surface of the liquid, with a stirring rod. Large amounts of K^+ influence the reaction; acids and NH_4^+ cause the separation of pyro-antimonic acid, $H_4Sb_2O_7$. Most of the other metals interfere. The reagent should be carefully prepared and dissolved when needed, as it does not form a stable solution.

7. **Ignition.** — Sodium bicarbonate, $NaHCO_3$, loses H_2O and CO_2 at about 100°, becoming Na_2CO_3.[6]

Sodium compounds color the flame intensely yellow, the color being practically unaffected by potassium (at full heat), but modified to orange red by much Li and readily intercepted by a cobalt glass.

The spectrum of sodium consists of two yellow bands (589.6mμ and 589.0mμ) seen as one line with spectroscopes of low resolving power.

[1] Schoorl, *Pharm. Weekblad*, **63**, 555 (1926), *C.A.* **20**, 2297; Meyerfeld, *Z. anal. Ch.*, **67**, 150 (1925), *C.A.* **20**, 1189.

[2] Kolthoff, *Ch. Weekblad*, **26**, 294–8 (1929), *C.A.* **23**, 3640; *Z. anal. Ch.*, **70**, 397–400 (1927), *C.A.* **21**, 1773.

[3] Kolthoff, *Pharm. Weekblad*, **60**, 1251–5 (1923), *C.A.* **18**, 510.

[4] Caley, *J. Am. Ch. Soc.*, **51**, 1965 (1929), *C.A.* **23**, 4160.

[5] Mathers, *et al.*, *J. Am. Ch. Soc.*, **37**, 1515–7 (1915).

[6] Caven and Sand, *J. Ch. Soc.*, **99**, 1367 (1911).

The amount of Na in the atmosphere and in the larger number of substances labeled "Chemically Pure" is ample to give a distinct but evanescent yellow to the flame and spectrum.[1,2]

8. Detection. — Sodium is usually detected by the color of the flame. This test is, however, not as easy as some writers would lead one to believe. The difficulty comes in distinguishing between Na intentionally added and that present merely as an impurity. Hence, where possible, the original unknown should be used for the flame test with the qualification that a solution gives a more delicate test than a solid. Sodium can also be detected by precipitation as the pyroantimonate (cf. 6, *g*) or as the uranyl acetate (6, *b*).

9. Determination. — Usually Na is determined by difference. After the removal of other metals, KCl and NaCl are precipitated and weighed together. The KCl is then separated, its weight ascertained and subtracted from that of the two. A direct determination of Na may be effected by precipitation and weighing as sodium zinc uranyl acetate,[3] or as sodium magnesium uranyl acetate.[4]

10. Oxidation and Reduction. — Sodium ranks with potassium as a very powerful reducing agent. It is not quite as violent in its reaction and being much cheaper, is almost universally used instead of potassium. Sodium peroxide may react either as a reducing or oxidizing agent, depending upon conditions. The action is similar to that of H_2O_2 in alkaline medium (p. 480).

§207. Ammonium (Gr. *ammos* = sand)[5] NH_4. Valence 1.

1. Physical Properties. — Density of NH_3 liquid at −34°, 0.677; solid at −79°, 0.817 g./cc.[6] The weight of a normal liter of NH_3 is 0.7717 g.[7] The liquid freezes at −77.7° and boils at − 33.41° ± 0.1°; has a vapor pressure of 9.9 atmospheres at 25°; burns in oxygen without heating. At room temperature ammonia is a gas with a very penetrating odor. It burns with a greenish-yellow flame, and combines energetically with acids to form salts, the radical NH_4^+ being univalent and acting in many respects like K^+ and Na^+. At 0° one volume of H_2O absorbs 1300 volumes of the gas; at 20°, 700 volumes. Large amounts of ammonia (as ammonium salts) are used as fertilizer and in explosives; aqua ammonia is used in washing and cleaning; liquid ammonia is used in refrigeration.

2. Occurrence. — Free ammonia does not occur in nature. Various ammonium salts are widely distributed in rain water, in many mineral waters, in almost all plants, among the products of decay or decomposition of nitrogenous organic bodies, etc.

[1] de Gramont, *J. ch. phys.*, **14**, 338 (1916).

[2] Kirchhoff and Bunsen, *J. prakt. Ch.*, **80**, 455 (1860), have reported the sensitivity of the flame test to be 1/3,000,000, mg. of Na.

[3] Barber and Kolthoff, *J. Am. Ch. Soc.*, **50**, 1625 (1928).

[4] Caley and Foulk, *J. Am. Ch. Soc.*, **51**, 1664 (1929).

[5] Possibly the name has some connection with that of the ancient temple of Jupiter-ammon.

[6] Bergstrom, *J. Phys. Ch.*, **26**, 876 (1922).

[7] Moles and Batuecas, *Monatsh.*, **53-4**, 779–85 (1929), *C.A.* **24**, 1264.

3. Preparation. — (1) Ammonia is obtained by interaction of H_2 and N_2 ($3\,H_2 + N_2 = 2\,NH_3$) in the presence of a catalyst. The Haber process uses reduced Fe_3O_4 at a temperature of 550–600° and a pressure of 100–200 atmospheres. The Claude process employs a distinctly higher temperature, i.e., 600–1000°. (2) Much ammonia is obtained as a by-product in the coking of coal. (3) Calcium carbide, if heated in N_2 to about 1200°, becomes calcium cyanamide, which reacts with steam to form NH_3 ($CaCN_2 + 3\,H_2O = 2\,NH_3 + CaCO_3$).

4. Hydroxide. — Ammonium hydroxide, NH_4OH, is made by passing ammonia, NH_3, into H_2O ($NH_3 + H_2O \rightleftarrows NH_4OH \rightleftarrows NH_4^+ + OH^-$). The gas is absorbed by the H_2O with avidity and a strongly alkaline solution is produced (see above). A solution having a specific gravity of 0.90 at 20° contains 26% NH_3. Probably the major part of this NH_3 is present as dissolved NH_3, only one-third combining with the solvent to form NH_4OH.[1] Calculated on the basis of total NH_3 present NH_4OH is ionized to the extent of 1.4% in 0.1 *N* solution. Its dissociation constant (K) is calculated to be $2.5\ 10^{-5}$.[2]

5. Solubilities. — Ammonia and all ammonium salts are soluble in H_2O. Ammonia dissolves less readily in a strong solution of KOH than in H_2O. The bicarbonate and phosphate are efflorescent. The nitrate and acetate are deliquescent, the sulfate slightly deliquescent.

6. Reactions. — *a.* The fixed alkali hydroxides and carbonates liberate ammonia, NH_3, from solutions of NH_4^+, in the cold, and more rapidly upon heating. Ammonium hydroxide, NH_4OH, volatile alkali, colors litmus blue, neutralizes acids, and precipitates positive ions of the first four groups and Mg^{++} (Mn^{++} and Mg^{++} incompletely). In the presence of sufficient ammonium salts no precipitate is obtained with Ag^+, Cu^{++}, Cd^{++}, Co^{++}, Ni^{++}, Zn^{++}, Mn^{++} and Mg^{++}. The precipitate is a hydroxide, except that with Ag^+ and Sb^{+3} it is the oxide, with Hg^{++} an ammoniated salt and with lead a basic salt. Addition of excess reagent dissolves the precipitate of Ag_2O, $Cu(OH)_2$, $Cd(OH)_2$, $Co(OH)_2$, $Ni(OH)_2$ and $Zn(OH)_2$ with formation of an ammonia complex. Ammonium carbonate, $(NH_4)_2CO_3$, is unstable changing to the carbamate, $NH_4NH_2CO_2$.[3] In solution, the carbonate precipitates positive ions of all the non-alkali metals, chiefly as carbonates (normal or basic) except Mg^{++} which is not affected in dilute solution. With Ag^+, Cu^{++}, Cd^{++}, Co^{++}, Ni^{++} and Zn^{++} the precipitate is dissolved by excess reagent.

b. Tartaric acid gives a precipitate with NH_4^+, corresponding to and very closely resembling potassium bitartrate. The ammonium salt is more soluble than the potassium salt and does not leave a carbonate residue upon ignition.

c. Sodium cobaltinitrite precipitates NH_4^+ the same as K^+ (§205, 6, *c*).

e. When NH_4OH is treated with H_2S, ammonium sulfide, $(NH_4)_2S$, is formed.[4] Freshly prepared $(NH_4)_2S$ is colorless, but on standing becomes

[1] See especially E. Baars: "The State of Ammonia in Aqueous Solution." Ahrens' Sammlung, Vol. 29 (**1927**).

[2] Sallinger, *Kolloidch. Beihefte*, **25**, 424–7 (1927), *C.A.* **23**, 16. This value is higher than most modern values which are nearer 1.8×10^{-5}.

[3] Burrows and Lewis, *J. Am. Ch. Soc.*, **34**, 993–5 (1912), consider the equilibrium between $(NH_4)_2CO_3$ and $NH_4NH_2CO_2$.

[4] With excess H_2S the product is more likely NH_4HS. This is also true if hydrolysis of the $(NH_4)_2S$ is not prevented.

yellow due to loss of NH_3 and formation of some polysulfide, $(NH_4)_2S_x$. The polysulfide may also be formed by dissolving sulfur in the normal $(NH_4)_2S$ (cf. §323). As a precipitating reagent $(NH_4)_2S$ resembles the fixed alkali sulfides. The sulfides of Sb^{+3} and Sn^{++} are readily soluble in $(NH_4)_2S_x$, but not in $(NH_4)_2S$. Nickel sulfide tends to form a colloidal solution in $(NH_4)_2S_x$.

f. Perchloric acid gives no precipitate with NH_4^+ (distinction from K^+).

g. A dilute solution of picric acid forms a bright yellow solution with NH_4OH. A precipitate of ammonium picrate[1] is formed if the solution is concentrated.

Fluosilicic acid, H_2SiF_6, does not precipitate NH_4^+ (distinction from K^+). Chloroplatinic acid, H_2PtCl_6, forms with NH_4^+ a yellow precipitate, $(NH_4)_2PtCl_6$, very closely resembling the potassium salt. Upon ignition, however, only the spongy Pt° is left, whereas with K_2PtCl_6 a residue of Pt° + KCl is obtained.

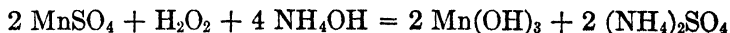
Nessler's reagent, alkaline K_2HgI_4, gives a pale yellow solution to brown precipitate when treated with NH_3, the depth of color depending upon the amount of NH_3:

$$NH_3 + 2\ K_2HgI_4 + 3\ KOH = NH_2IHg_2O + 7\ KI + 2\ H_2O$$

The precipitate is soluble in excess KI and in HCl. This is a very delicate test, applicable to any ammonium compound that will evolve NH_3. An important feature of the test is that the NH_3 is conducted into the reagent thus eliminating interference by other ions present in the sample being examined. Of course, if no ions are present that give a precipitate with the reagent it may be added directly to the unknown solution. Cyanides, sulfides and bicarbonates interfere with this test.

Mercuric chloride, $HgCl_2$, forms in solutions of NH_4OH or $(NH_4)_2CO_3$ a white precipitate of amino mercuric chloride, NH_2HgCl. (If the carbonate is present the precipitate is similar to that obtained with Nessler's reagent, NH_2ClHg_2O.) If NH_3 is not present in the solution being tested it may be liberated from the NH_4^+ by addition of $HgCl_2$ and Na_2CO_3 previously mixed in solution so dilute as not to form a precipitate of mercuric oxide (yellow). This test is claimed by some workers to be as delicate as Nessler's test, revealing the presence of NH_3 derived from the air by water.[2]

If a filter paper is wet with a solution of $MnSO_4$ and H_2O_2, then held in NH_3 gas, a brown color will develop due to oxidation of the Mn by H_2O_2 in the alkaline medium thus formed:

$$2\ MnSO_4 + H_2O_2 + 4\ NH_4OH = 2\ Mn(OH)_3 + 2\ (NH_4)_2SO_4$$

[1] This compound is used as an explosive.

[2] Wittstein, *Arch. Pharm.*, [3] **3**, 397 (1873). Cf. de Koninck, *Ch. News*, **69**, 220 (1894), who states that alcohol does not interfere.

Sodium phosphomolybdate precipitates NH_4^+ from neutral or acid solutions, also the other fixed alkalis except Na^+ and Li^+.

As little as $0.0_6 34$ g. of NH_3 may be detected by the film mirror that it produces on a drop of $AgNO_3$ solution containing 3% CH_2O.[1] Tannin may be used in place of the CH_2O.[2]

7. **Ignition.** — Heat vaporizes the carbonate and the halide salts of NH_4^+ undecomposed (dissociated in presence of moisture but reuniting upon cooling); decomposes the nitrate with formation of N_2O and H_2O, and phosphate and borate with evolution of NH_3.

8. **Detection.** — *a.* Since ammonium compounds are used in the regular process of analysis, the original solution must be tested for NH_4^+. The hydroxide or the carbonate may be detected by the odor; the action on red litmus paper suspended in the test tube above the heated liquid; the blue color imparted to paper wet with $CuSO_4$; the blackening of $Hg_2(NO_3)_2$-paper or of $MnSO_4+H_2O_2$-paper; (if in considerable quantity) the white "smoke" when brought in contact with the vapor of volatile acids, e.g., HCl. Practically all other ammonium salts must be treated with a fixed alkali hydroxide or carbonate (oxides or hydroxides of Ba, Sr, or Ca may be used) and the NH_3 thus liberated distilled into Nessler's reagent, or collected in H_2O and detected by any of the above tests.

b. Organic reagents suggested for the detection of NH_4^+ are:

(1) "Tetra" (tetramethyldiaminodiphenylmethane) gives a purple color with 0.01–0.02 mg. of NH_3.[3] (2) An ammonium salt mixed with 4% phenol then treated with dilute NaClO gives a blue color.[4] (3) If NH_4^+ is well shaken with *p*-diazonitraniline and then 10% NaOH added dropwise the agitated liquid becomes yellow to red.[5, 6]

9. **Determination.** — Ammonium salts are usually determined *volumetrically* by distillation into a standard acid from a solution alkaline with NaOH and titration of the excess acid with standard alkali using methyl red or cochineal as an indicator. Absorption of the NH_3 in a solution of boric acid and titration with standard acid is one of the modifications suggested by several investigators. Very small amounts of NH_3 are usually determined *colorimetrically* by absorption in Nessler's reagent and comparison with samples containing known quantities. *Gravimetrically*, NH_3 may be determined by precipitation as $(NH_4)_2PtCl_6$ and weighing as such. This method is seldom used.

10. **Oxidation and Reduction.** — Ammonia and ammonium compounds tend to form very unstable (explosive) products with a large number of substances. While the intermediate products may vary according to conditions in general, the final stage is nitrogen, N_2. Ammonium salts in

[1] Zenghelis, *Compt. rend.*, **173**, 153 (1921), *C.A.* **15**, 3432.
[2] Makris, *Z. anal. Ch.*, **81**, 212–4 (1930), *C.A.* **24**, 4731.
[3] Carney, *J. Am. Ch. Soc.*, **34**, 32–5 (1912).
[4] Thomas, *Bull. soc. ch.*, **11**, 796–9 (1912), *C.A.* **6**, 3241 (1912).
[5] Riegler, *Ch. Ztg.*, **21**, Rep. No. 36, p. 307 (1897).
[6] Cf. Gutzeit, *Helv. Ch. Acta*, **12**, 713–40 (1929), *C.A.* **23**, 4644.

strong acids treated with Cl_2 (or ClO^-) form "nitrogen chloride," NCl_3[1] (very unstable) (Eq. 1, 2). In dilute acid solution the NCl_3 becomes N_2 (Eq. 3). Dilute equimolar solutions of NH_3 and HClO form chloramine (Eq. 4). Ammonia and Br_2 in fixed alkaline solution form N_2 (Eq. 5). The same is, of course, true with ClO^- or BrO^- (Eq. 6). With iodine and NH_4OH nitrogen iodide, $NI_3 \cdot NH_3$ (very explosive), is produced (Eq. 7); under certain conditions an iodate may be obtained (Eq. 8). So-called fulminating gold or silver is obtained by adding NH_4OH and NaOH to a solution of the metal ion. Ammonium hydroxide may be oxidized by the air to NH_4NO_2 and NH_4NO_3. Ammonia gas, in the presence of Pt° as a catalyst at *ca.* 900°, is oxidized to NO (Eq. 9). Permanganates oxidize NH_3 to NO_3^- (Eq. 10). Ammonia is readily produced from nitrates by strong reducing agents (Eq. 11). It is obtained along with CO_2 from an aqueous solution of HCNO and more slowly from HCN. It is also generated by fixed alkalis in boiling cyanide solutions. Fusion with fixed alkalis transforms all the nitrogen of organic bodies into ammonia.

(1) $NH_4Cl + 3\ Cl_2 = NCl_3 + 4\ HCl$
(2) $NH_4Cl + 3\ HClO = NCl_3 + HCl + 3\ H_2O$
(3) $NCl_3 + NH_4Cl = N_2 + 4\ HCl$
(4) $NH_3 + HClO = NH_2Cl + H_2O$
(5) $2\ NH_3 + 3\ Br_2 + 6\ NaOH = N_2 + 6\ NaBr + 6\ H_2O$
(6) $2\ NH_3 + 3\ NaClO = N_2 + 3\ NaCl + 3\ H_2O$
(7) $2\ NH_3 + 3\ I_2 + 3\ NH_4OH = NI_3 + NH_3 + 3\ NH_4I + 3\ H_2O$
(8) $6\ NH_4OH + 3\ I_2 = 5\ NH_4I + NH_4IO_3 + 3\ H_2O$
(9) $4\ NH_3 + 5\ O_2 = 4\ NO + 6\ H_2O$
(10) $6\ NH_4OH + 8\ HMnO_4 = 3\ NH_4NO_3 + 8\ MnO(OH)_2 + 5\ H_2O$
(11) $3\ NaNO_3 + 8\ Al + 5\ NaOH + 2\ H_2O = 3\ NH_3 + 8\ NaAlO_2$

§208. Cesium (L. *coesius* = sky blue). Cs = 132.81. Atomic No. 55. Valence 1. Discovered by Bunsen[2] in 1860.

1. Physical Properties. — Density, 1.87;[3] melting point, 29.7°;[4] boiling point, 670°. Cesium is similar to the other alkali metals; it is silvery white, ductile and probably the softest of all the metals. It melts on exposure to the air due to absorption of impurities and ultimately takes fire, burning with a reddish-violet flame to form the oxide. In oxygen it ignites at room temperature. It takes fire when thrown on water. It may be kept under kerosene. It is the most electro-positive of all metals (No. 87 not being considered). Recently Cs was believed to be an excellent metal for use in radio tubes, but subsequent tests showed others better.

[1] Bray and Dowell, *J. Am. Ch. Soc.*, **39**, 905–13 (1917).
[2] Spectroscopically in the spring waters of Dürkheim. This is a good example of the delicacy of the spectroscopic test, because later Bunsen found it necessary to evaporate 40 tons of the water in order to secure sufficient Cs for study.
[3] Richards and Brink, *J. Am. Ch. Soc.*, **29**, 117 (1907).
[4] Bridgeman, *Proc. Am. Acad. Arts Sci.*, **60**, 385–421 (1925), *C.A.* **20**, 698.

2. Occurrence. — Cesium is widely distributed in small quantities but commercially available deposits are curiously concentrated. One is found in Maine, another in the Black Hills, and a third in the island of Elba. The principal minerals are pollucite, $Cs_4Al_4H_2Si_9O_{27}$, and lepidolite, $(Li,K,)_2(F,OH)_2Al_2Si_3O_9$, cesium being present in place of some of the alkali indicated. Certain mineral waters contain traces of Cs.

3. Preparation. — Cesium has been prepared by electrolysis of a mixture of CsCN and $Ba(CN)_2$. It may also be obtained by reduction of CsOH with Al or Mg or anhydrous CsCl with metallic Ca.[1]

4. Oxides and Hydroxide. — Cesium oxide, Cs_2O, red, is obtained by careful ignition of the metal.[2] It absorbs moisture and CO_2 from the air, becoming white Cs_2CO_3 (see 1 above). In water Cs_2O forms the corresponding hydroxide, CsOH, the reaction being highly exothermic. Cesium hydroxide, CsOH, is very deliquescent and like the other alkali hydroxides dissolves in H_2O with the liberation of much heat. A number of higher oxides have been reported (Cs_2O_2, Cs_2O_3, Cs_2O_4) as well as certain sub-oxides (Cs_7O, Cs_4O, Cs_3O, etc.).

5. Solubilities. — Cesium dissolves, with great energy in H_2O, acids or alcohol, liberating H_2 and forming the hydroxide, salt, or alcoholate, respectively. The hydroxide is readily soluble in H_2O (79.4 g./100 g. of solution at 15°) and alcohol. The ordinary salts are all readily soluble, the chloroplatinate, Cs_2PtCl_6, the bitartrate, $Cs_2HC_4H_4O_6$, and the silicotungstate, $Cs_8SiW_{12}O_{42}$, being least soluble (§209, 5).

6. Reactions. — In all reactions Cs is similar to the other alkali metals, particularly potassium (§209).

7. Ignition. — Cs salts color the non-luminous Bunsen flame violet. The spectrum shows two sharply defined lines in the blue (Csα, 455. 5mμ and Csβ, 459.3mμ) and a third, fainter line in the orange red (Csγ, 601.6mμ). The spectroscopic test is very delicate (see above).

8. Detection. — Cesium is usually detected spectroscopically (cf. 7).

9. Determination. — Cesium may be determined by the methods described under potassium, i.e., as $CsClO_4$, Cs_2PtCl_6, etc. Methods for the separation of Cs, Rb and K are apparently unsatisfactory from a quantitative standpoint.[3]

§209. Rubidium (L. *rubidus* = red). Rb = 85.44. Atomic No. 37. Valence 1. Discovered by Bunsen in 1860.

1. Physical Properties. — Density, 1.52°;[4] melting point 38.7°;[5] boiling point, 700°. Rubidium is a silvery white metal, soft as wax at −10°. It oxidizes rapidly in the air, developing much heat and soon igniting. It volatilizes as a blue vapor below a red heat. The metal does not keep well under kerosene being best preserved in an atmosphere of hydrogen. Next to cesium it is the most electro-positive of all the metals.

2. Occurrence. — Rubidium is widely distributed in small quantities usually with the other alkali metals, but not in the same mineral with Cs. Lepidolite may contain as high as 1% Rb. Certain mineral waters also contain this element (§208, 2). If a demand arises it can be recovered commercially as a by-product of the Stassfurt salt industry.

3. Preparation. — Rubidium may be recovered from the mother liquor obtained (1) in the preparation of Li salts, (2) in the removal of KCl from carnallite. It is also prepared by electrolysis of the cyanide or fused chloride or by heating the anhydrous chloride with metallic Ca.[6]

[1] Cf. de Boer, *et al., Z. anorg. allgem. Ch.*, **160**, 128 (1927); Hackspill, *Ann. ch. phys.*, [8] **28**, 613 (1913).

[2] Rengade, *Compt. rend.*, **143**, 592, 1152 (1906); **144**, 753 (1907), *C.A.* **1**, 1527; *Ann. ch. phys.*, [8] **2**, 348–432 (1907), *C.A.* **2**, 28.

[3] Hillebrand and Lundell, p. 529.

[4] Hackspill, *Compt. rend.*, **152**, 259 (1911).

[5] Bridgeman, *Proc. Am. Acad. Arts Sci.*, **60**, 385 (1925), *C.A.* **20**, 698.

[6] Hackspill, *Ann. ch. phys.*, [8] **28**, 613 (1913); cf. de Boer, *et al., Z. anorg. allgem. Ch.*, **160**, 128 (1927).

4. Oxides and Hydroxide. — Rubidium oxide, Rb_2O, pale yellow, is obtained along with RbO_2 (?), by careful ignition of the metal.[1] Rubidium hydroxide, RbOH, is formed when the metal interacts with H_2O. Like the other fixed alkalis it is deliquescent and readily soluble in water. Higher oxides, as Rb_2O_2, Rb_2O_4, etc., have been reported.[2]

5. Solubilities. — The metal dissolves in cold H_2O, in acids and in alcohol with great energy, evolving H_2. The hydroxide dissolves in H_2O to the extent of 36.4 g./100 g. of solution at 30°. The salts are all readily soluble. Table 38 shows the solubility of the less soluble salts of K, Rb and Cs in water.

TABLE 38

SOLUBILITY OF SOME POTASSIUM, RUBIDIUM AND CESIUM SALTS IN WATER

	K	Rb	Cs
Chloroplatinate at 10°	0 9*	0 154	0 050
at 100°	5.22	0.634	0.377
Acid tartrate at 25°	0.37 (0°)	1.18	9.7
at 100°	6.1	11.7	98 0
Perchlorate	0.7 (0°)	1.09 (21°)	given as insol.
Fluosilicate	0.12 (17.5°)	0.16 (20°)	60 (17°)
Periodate	0.66 (13°)	0.65 (13°)	2 15 (15°)
Permanganate	2.83 (0°)	0.46 (0°)	0.097 (1°)

* Solubility is given in grams of salt per 100 g. of water at the temperature stated.

6. Reactions. — Similar to the other fixed alkalis (cf. 8).

7. Ignition. — The salts of Rb impart a violet color to the non-luminous flame. The spectrum shows two distinguishing lines in the violet (Rbα, 420.2mμ; Rbβ, 421.6mμ) two in the red that are more characteristic (Rbγ, 620.7mμ and Rbδ 629.9mμ); a fifth in the orange and several others in the orange, yellow and green. The test is very delicate, 0.0_62 g. being readily detectable.[3]

8. Detection. — The spectroscope offers the most satisfactory means. Where precipitation methods are required the following will be helpful:

(*a*) From the figures in 5 above, it would appear that a good way to precipitate Cs^+ in the presence of K^+ would be to use MnO_4^-; K^+ and Rb^+ in the presence of Cs^+ would be to use SiF_6^{--}. Temperature plays an important part, however, so that other ways have been advocated for separating these closely related alkali metals.

(*b*) K^+ and Rb^+ are separated from Cs^+ by means of $HC_4H_4O_6^-$.

(*c*) Cs^+ is precipitated as $3CsCl{\cdot}2SbCl_3$ by addition of $SbCl_3$ in concentrated HCl. All other alkali metal ions including NH_4^+ remain in solution.[4]

(*d*) Cs^+ is precipitated by $SnCl_4$ from a concentrated HCl solution as Cs_2SnCl_6. This is a separation from all but NH_4^+.

(*e*) K^+, Rb^+ and Cs^+ may be precipitated together as perchlorates, converted to the cobaltinitrites, and decomposed to the simple nitrites by ignition with $NaNO_2$. Solution

[1] There is some question as to whether the pure monoxide has been prepared.

[2] Rengade, *Compt. rend.*, **144**, 920 (1907), *C.A.* **1**, 1830.

[3] Bunsen, *Ann.*, **125**, 367 (1863).

[4] Godeffroy, *Ber.*, **7**, 375 (1874); Strecker and Diaz, *Z. anal. Ch.*, **67**, 321–41 (1925), *C.A.* **20**, 1366, discuss accuracy of the method. Cf. Moser and Ritschel, *Z. anal. Ch.*, **70**, 184 (1927).

of the residue and precipitation of the Cs^+ and Rb^+ as the triple nitrites,[1] $Cs_2NaBi(NO_2)_6$ and $Rb_2NaBi(NO_2)_6$, leaves K^+ in the filtrate to be detected as the cobaltinitrite. The precipitate of triple nitrites is dissolved, Bi^{+3} removed, and the Cs^+ precipitated as indicated in (*c*) or (*d*). The Sb or Sn is removed from the filtrate and the Rb^+ precipitated as $RbHC_4H_4O_6$ or better, by means of sodium chloronitrotoluenemetasulfonate.[2] If necessary, traces of Cs^+ may be removed from the final filtrate by means of silicotungstic acid.[3]

(*f*) Sodium ferrocyanide in presence of $CaCl_2$ gives a precipitate with aqueous solutions containing Rb^+ or Cs^+; K^+ and NH_4^+ are precipitated only from a solution containing 50% alcohol; Na^+ and Li^+ are not affected.[4, 5]

9. Determination. — *a.* Probably the simplest way to determine Rb is to compare the spectrum with that of a sample containing a known amount of the metal.

b. A satisfactory gravimetric method for the separation and determination of K, Rb and Cs is yet to be discovered. About the nearest approach involves the steps described in 8, *f*.[6]

§210. Lithium (Gr. *lithos* = stone). Li = 6.940. Atomic No. 3. Valence 1. Discovered by Arfvedson in 1817.

1. Physical Properties. — Density, 0.534°;[7] the lightest metal known; melting point 186°;[8] boiling point, 1200°[9] (volatilizes at a bright red heat). Lithium is a silvery white metal, harder than Na or K, but softer than Pb, Ca or Sr. It is tough and may be drawn into wire or rolled into sheets. It is more electro-positive than the alkaline earth metals, but less so than Na and K. The pure metal is similar in appearance and chemical properties to Na and K, but does not react as violently as they do. It does not ignite in the air until heated to 200°, and then burns quietly with a very intense white light. It also burns brilliantly in Cl_2, Br_2, I_2, O_2, S and dry CO_2. It decomposes H_2O readily forming LiOH and H_2, but not with combustion of the hydrogen or the metal. Metallic Li is prepared on a commercial scale at a cost of about $2.50 per pound for 98%–99% metal. It may be used in various alloys, chiefly as a hardener; e.g., Pb-Ca-Li bearing metal; Al-Li ("Scleron") is considered an excellent substitute for brass. The Li is present, of course, only in small amount. The compounds are used to some extent in glass, medicine and fireworks.

2. Occurrence. — Lithium occurs in the outer portion of the earth to the extent of about 0.01%. It is widely scattered, commercial deposits being exploited in Saxony, France, Canada (Manitoba and Quebec) and the United States (large deposits in South Dakota, Arizona, California and New Mexico). The most important minerals are: lepidolite or lithium mica, $(Li,K)_2(F,OH)_2 \cdot Al_2Si_3O_9$, containing 1%–3% Li; spodumene, $LiAl(SiO_3)_2$, 3.8% Li; amblygonite, $AlPO_4 \cdot LiF$, 8%–10% Li.

3. Preparation. — Lithium minerals are digested with concentrated HCl and the Li recovered as the carbonate after the removal of other metals. The metal itself may be obtained by electrolysis of the fused chloride containing KCl. Ignition of

[1] Ball, *J. Ch. Soc.*, **95**, 2126–30 (1909), *C.A.* **4**, 883.

[2] Davies, *J. Ch. Soc.*, **123**, 2976 (1923).

[3] The above method for the detection of 1 mg. of either element in the presence of 100 mg. of the other is that of Noyes and Bray, p. 248 *et seq.*

[4] Gaspar y Arnal, *Anales soc. españ. fís. quim.*, **24**, 99, 150 (1926), *C.A.* **20**, 2297.

[5] Characteristic compounds of Cs and Rb are described by Missenden, *Ch. News*, **124**, 362 (1922), *C.A.* **16**, 2820.

[6] See Hillebrand and Lundell, p. 529, E.

[7] Richards and Brink, *J. Am. Ch. Soc.*, **29**, 117 (1907).

[8] B. Stds. Cir. 35.

[9] Mellor, II, p. 457, Table 3, gives + 1400°.

the carbonate with Mg is less satisfactory, because the Li is volatilized and quickly oxidized.[1]

4. Oxides and Hydroxide. — Lithium oxide, Li_2O, is obtained by heating the metal in O_2 or dry air or by fusion of the nitrate. (The first method gives some Li_2O_2 also.) The oxide slowly dissolves in H_2O to form lithium hydroxide, LiOH. It can also be readily prepared by treating Li_2SO_4 with $Ba(OH)_2$. In general properties it is similar to the other alkali hydroxides.[2] Appreciable amounts of Li_2O_2 are not obtained upon heating the metal in oxygen (distinction from Na). The peroxide is best obtained by treatment of an aqueous solution of LiOH and H_2O_2 with alcohol, and dehydration of the precipitate.

5. Solubilities. — The metal is readily soluble in H_2O with evolution of H_2 and formation of LiOH; soluble in acids with formation of salts. The oxide, Li_2O, dissolves in H_2O, forming the hydroxide. The solubility of LiOH is 11.3 g./100 g. of solution at 10°, increasing to about 15 g. at 100°. Most of the Li salts are soluble in H_2O. A number of them, including LiCl and $LiClO_3$, are very deliquescent. The hydroxide, carbonate (1.5 g./100 g. of solution at 0°) and phosphate, Li_3PO_4 (0.04 g./100 g. of solution),[3] are less soluble in H_2O than the corresponding compounds of the other alkali metals. In this respect Li shows an approach to the alkaline earth metals. Lithium phosphate is more soluble in NH_4Cl than in H_2O. Lithium fluoride is also only slightly soluble in water (0.26 g./100 g. of solution at 18°). Lithium chloride is soluble in alcohol. The solubility of Li_2SO_4 is 25.85 g./100 g. of solution at 19.6°.[4]

6. Reactions. — Lithium salts, in general, react similar to the corresponding K and Na salts. They are as a rule more fusible and more easily decomposed upon fusion. Soluble phosphates precipitate lithium phosphate, more soluble in NH_4Cl than in H_2O alone (distinction from Mg). In dilute solutions the phosphate is not precipitated until the solution is boiled. The delicacy of the test is increased by the addition of NaOH, forming a double phosphate of Na and Li. The phosphate dissolved in HCl is not at once reprecipitated upon neutralization with NH_4OH (distinction from the alkaline earth metals). Chloroplatinic and tartaric acid do not precipitate Li from dilute solution (distinction from K, Rb, Cs). Li^+ is precipitated by de Koninck's cobaltinitrite reagent.[5] Ammonium fluoride, in excess, precipitates LiF only. The separation is more complete from ammoniacal solution.

7. Ignition. — Compounds of Li impart to the non-luminous flame a carmine red color, obscured by Na, but not by small quantities of K. Cobalt glass, thick enough to cut off the yellow light of Na, transmits the red light of Li, thus interfering with the test for K. The spectrum of Li consists of a beautiful red band, Liα (670.82mμ), and a faint orange line, Liβ (610.38mμ).

8. Detection. — The spectroscope offers the best means for detection of Li. The dry chlorides of the alkali metals are moistened with a few drops of HCl and then extracted with alcohol. The solution contains all the rare alkalis and some Na^+ and K^+. Removal of the alcohol and precipitation of K^+, Rb^+ and Cs^+ from aqueous solution leaves a filtrate of Na^+ and Li^+. This filtrate is treated with oxalic acid, dried, the residue ignited, moistened with HCl and extracted with absolute alcohol and ether. Upon evaporation of the extract LiCl is obtained almost pure. It may be tested with the spectroscope and by precipitation as the phosphate.[6] The method of Noyes and Bray[7] separates Na^+ and Li^+ from K^+, Rb^+ and Cs^+ by precipitation of the latter as perchlo-

[1] Cf. Hackspill, *Ann. ch. phys.*, [8] **28**, 613 (1913). Braun, *Metallbörse*, **19**, 2637–9 (1929), *C.A.* **24**, 560, gives a review, with bibliography, for the preparation of metallic lithium.

[2] The Edison storage battery electrolyte contains 5% LiOH to increase its capacity.

[3] Cf. Rosenheim and Reglin, *Z. anorg. allgem. Ch.*, **120**, 109 (1922).

[4] Friend, *J. Ch. Soc.*, **1929**, 2330–3, *C.A.* **24**, 1565.

[5] de Koninck, *Z. anal. Ch.*, **20**, 390 (1881).

[6] Caley, *J. Am. Ch. Soc.*, **52**, 2754–8 (1930), suggests that LiCl be extracted from a mixture of the chlorides by digestion with amyl alcohol followed by precipitation of the Li as the stearate.

[7] Noyes and Bray, p. 245 *et seq.*

rates from an alcoholic solution.[1] The filtrate containing Na^+ and Li^+ is saturated with HCl gas to remove Na^+ as NaCl. The filtrate is diluted with H_2O and (very cautiously!!)[2] evaporated on a steam bath, and Li^+ ultimately precipitated as the phosphate from a strongly ammoniacal solution containing alcohol.[3]

9. Determination. — Lithium may be determined by the comparative intensity of the lines in the spectrum.[4] *Gravimetrically*, Li is precipitated and weighed as the sulfate, Li_2SO_4,[5] or phosphate, Li_3PO_4.

§211. Outline of the Analysis of Group VI

(Starting with the filtrate from Group V)

Metals not precipitated by the reagents used for Groups I–V

Metals	Mg	Na	K	(NH_4)
Ions in acid or alkaline solution	Mg^{++}	Na^+	K^+	NH_4^+

Remove traces of Group V metals with $(NH_4)_2SO_4$ and $(NH_4)_2C_2O_4$

Mg^{++}	Na^+	K^+	NH_4^+
Divide into 2 parts			Test original soln.
$(NH_4)_2HPO_4$	flame test	flame test	$NaOH$ + heat
$\underline{MgNH_4PO_4}$	Also apply flame test on original solution.		$NH_3 \uparrow$

DIRECTIONS FOR THE ANALYSIS OF THE SIXTH GROUP

Group VI consists of those metals not precipitated by the earlier group reagents. It includes Mg, Na and K, among the more common metals, and the ammonium radical, NH_4^+. Of the cations, only Mg^{++} forms an appreciable number of precipitates with ordinary reagents. For the others, while precipitation reactions are available, the separations necessary to

[1] Cf. Willard and Smith, *J. Am. Ch. Soc.*, **45**, 293 (1923); Smith, G. F., *Ibid.*, **47**, 762 (1925); Smith and Ross, *Ibid.*, **47**, 774, 1020 (1925).

[2] Ample care should be taken to guard against injuring anyone should an explosion occur.

[3] Cf. Ato and Wada, *Sci. Papers Inst. Phys. Ch. Res. (Japan)*, **4**, 263–93 (1926); Gmelin, 8th ed., No. 20, p. 62 *et seq.*

[4] Skinner and Collins, U. S. Dept. Agr., Bur. Ch., Bull. No. 153; Bell, *Am. Ch. J.*, **7**, 35 (1886).

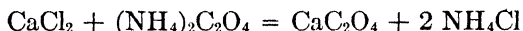
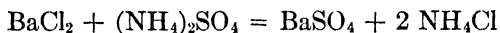
[5] Hillebrand and Lundell, p. 526.

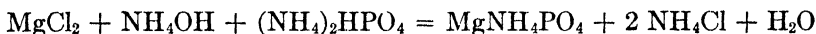
avoid interferences involve sufficient difficulties to lead usually to the adoption of other types of tests for these substances.

In the directions given below it is assumed that Groups I–V have been present and removed in the usual manner. If one wishes to examine a solution directly for Group VI, with Groups I–V known to be absent, portions of the original solution may be tested directly as indicated below. In the case of Mg^{++} the solution must be treated with NH_4Cl and NH_4OH as well as with $(NH_4)_2HPO_4$.

§211a. **Manipulation.** — To the major portion of the filtrate from Group V (p. 410) add 1–2 cc. each of $(NH_4)_2SO_4$ and $(NH_4)_2C_2O_4$, heat to boiling, and let stand 5–10 minutes. If a precipitate forms (see p. 411, note 3) filter and discard.

$$BaCl_2 + (NH_4)_2SO_4 = BaSO_4 + 2\ NH_4Cl$$

$$CaCl_2 + (NH_4)_2C_2O_4 = CaC_2O_4 + 2\ NH_4Cl$$

To the clear filtrate add 1–2 cc. of $(NH_4)_2HPO_4$, cool, and shake. A white crystalline precipitate forms if Mg is present.

$$MgCl_2 + NH_4OH + (NH_4)_2HPO_4 = MgNH_4PO_4 + 2\ NH_4Cl + H_2O$$

§212. **Notes.** — 1. The reagent used for the precipitation of Mg gives precipitates with most of the metals of the earlier groups. Therefore the accuracy of the test for Mg depends to a considerable extent on the completeness with which the earlier groups have been precipitated. The interfering metals that carry over into Group VI most commonly are Mn, Ba, Sr and Ca. The colloidal character of MnS makes it difficult to remove by filtration in Group IV, and the presence of too much NH_4Cl may cause the precipitation of Group V to be incomplete. The latter situation may be taken care of as indicated above, but the only way to make certain that the Mn is not interfering with the test for Mg is to test the final precipitate for Mn. This may be done by filtering, washing thoroughly, dissolving in HNO_3, and trying the action of Pb_3O_4, or $K_2S_2O_8 + AgNO_3$, as in Group IV. If Mn is present, the separations must be repeated on a fresh portion of the original solution.

2. Magnesium ammonium phosphate is appreciably soluble in warm water, therefore the solution must be cold in order to get reasonable precipitation of small amounts of Mg.

3. With only small amounts of Mg present, the precipitate may form very slowly due to supersaturation effects. In such a case the situation may be helped considerably by stirring the solution with a glass rod in such a way as to scrape the walls of the test tube or beaker. This starts crystallization on the scraped surface, and the condition of supersaturation disappears fairly promptly.

§213. **Manipulation.** — Try the flame test on a portion of the filtrate from Group V (p. 410; cf. p. 432). A bright yellow flame indicates the presence of Na. A violet colored flame indicates the presence of K. If a yellow flame is obtained, repeat the test for K, watching the flame through a cobalt glass. If K is present a reddish-violet flame will be observed.

§214. **Notes.** — 1. Sodium is one of the four impurities (Na, Fe, NH_4 and Cl) which are almost universally present in unknown materials, and for which the tests are of high delicacy. Because of this, one usually obtains a more or less distinct flame test

for Na on most of the solutions tested. If, however, a series of NaCl solutions are prepared, of decreasing concentrations, it will be found comparatively easy to distinguish between a solution containing a few tenths of a milligram of Na in 10 cc. and one containing 3–4 mg. Since the former represents the maximum amount usually present as impurity, one may adopt the somewhat arbitrary rule of considering that Na is not present as an intentionally added constituent if the flame test is less marked than that given by the test solution containing 3–4 mg. in 10 cc.

2. Since Na may be introduced into the solution by dust from the air, or by slight leaching of the surface of glass apparatus, it happens frequently that the flame test applied on the filtrate from Group V is more pronounced that that tried on the original solution. In such a case, the decision should be based on the results obtained on the original solution. If the original solution contains other materials giving flame colors whose brightness might interfere with the recognition of small amounts of Na, a portion of the original solution may be treated with NH_4OH, $(NH_4)_2CO_3$, and H_2S, the precipitate being discarded and the filtrate used directly for the flame test for Na (and K).

3. A precipitation test for Na that has been developed recently uses $UO_2(C_2H_3O_2)_2$ in a dilute acetic acid solution containing a high concentration of $Mg(C_2H_3O_2)_2$ (or of $Zn(C_2H_3O_2)_2$) the Na precipitating as a triple acetate, $NaMg(UO_2)_3(C_2H_3O_2)_9 \cdot nH_2O$. To 5 cc. of the solution to be tested (filtrate from Group V) add 5 cc. of the reagent and 1 cc. of alcohol. Stir if necessary to start crystallization. A greenish-yellow crystalline precipitate indicates Na. (A blank should be run as in Note 1.)

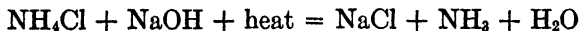
4. In using a cobalt glass to " filter " the yellow sodium flame, it is important to check the available glass against known solutions of NaCl and KCl and mixtures of the two containing relatively large amounts of Na and small amounts of K (100 mg. Na and 2–3 mg. of K in 10 cc.) to make sure of its effectiveness. Occasionally blue glasses are found that prove worthless when tested with known solutions. A true cobalt glass (made with cobalt oxide as a constituent of the glass) has high absorptive power for the yellow portion of the spectrum in which the sodium lines lie, but only slight absorptive power in the blue to violet end of the spectrum where the potassium lines lie. Other substances may be used in place of a cobalt glass; e.g., a plate of clear glass coated with a methyl violet film, or a glass cell containing a layer (about 2–3 cm. thick) of a nearly saturated solution of chrome alum, $KCr(SO_4)_2 \cdot 12H_2O$.

5. The precipitation reactions chiefly employed in the identification of K^+ are interfered with by NH_4^+. Therefore it is necessary, before they can be used, to evaporate the solution to dryness and remove ammonium salts by gentle ignition, cool and dissolve the residue in a little water.

To the solution thus prepared add 2–3 cc. of $Na_3Co(NO_2)_6$ solution, stir or shake, and look for the formation of a bright yellow precipitate, $K_2NaCo(NO_2)_6$. The reagent is somewhat unstable and should be tested with a known solution occasionally.

§215. Manipulation. — The test for NH_4^+ is made on the original solution, since NH_4OH and NH_4^+ salts are added in the regular schemes of group separation. Place 3–5 cc. of NaOH in a casserole and heat to boiling. Remove the flame, pour into the solution 1–2 cc. of the unknown, and quickly cover with a watch glass on the under side of which is stuck a strip of moist red litmus paper. If NH_4^+ is present the litmus paper will turn blue.

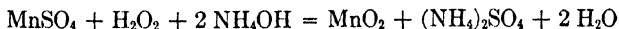
$$NH_4Cl + NaOH + \text{heat} = NaCl + NH_3 + H_2O$$

$$NH_3 + H_2O = NH_4OH$$

§215a. Notes. — 1. This test depends upon the instability of NH_4OH and the readiness with which NH_3 diffuses out of the hot solution, a property that was responsible for the name " volatile alkali " which distinguishes NH_4OH from the " fixed " alkalis. The NH_3 dissolves in the water that moistens the litmus paper (or condenses on the watch glass and runs down onto the litmus paper), reacting with it to form NH_4OH

which turns the solution alkaline and affects the indicator. In using the test it is important to see that no spray from the solution (from boiling or other formation of gas bubbles in the solution) strikes the litmus paper, otherwise the test paper may turn blue due to the NaOH carried in the spray.

2. The characteristic odor of NH_3 may be used to identify this gas in the fumes escaping from the alkaline solution. This test is less delicate than the litmus paper test, and cannot be relied on even for moderately dilute solutions unless the student first makes sure of his own ability to recognize the odor in the lower ranges of concentration which he expects to study (1–2 mg. in 10 cc.).

3. Another interesting test for NH_3 carries out the above procedure, but replaces the litmus paper with a piece of filter paper that has been moistened with a few drops of $MnSO_4$–H_2O_2 solution. Hydrogen peroxide does not affect a neutral $MnSO_4$ solution, but if the solution becomes alkaline from absorption of NH_3, the H_2O_2 readily oxidizes the Mn with formation of a tan to brown stain of MnO_2.

$$MnSO_4 + H_2O_2 + 2\,NH_4OH = MnO_2 + (NH_4)_2SO_4 + 2\,H_2O$$

4. One of the more delicate tests for NH_3 makes use of Nessler's reagent, a strongly alkaline solution of K_2HgI_4. If NH_3 is distilled into this solution a reddish-brown precipitate forms, OHg_2NH_2I. With very small amounts of NH_3 a tan colored solution is obtained. This may be matched with a standard whose concentration is known and the actual amount of NH_3 estimated. The chief difficulty with the test in the ordinary solution lies in the fact that NH_4OH solutions in the room lose NH_3 which diffuses into the air and contaminates other solutions. Also the film that quickly becomes visible on the bottles and windows in a qualitative analysis laboratory consists largely of NH_4Cl. Therefore it is difficult to prepare and to preserve a nearly colorless solution of Nessler's reagent. Further, since the test is one of considerable delicacy, indications of NH_3 will be obtained on practically all solutions tested. However, unless the solution becomes reddish brown in color the amount of NH_3 indicated may be considered as impurity in the solution, probably introduced in the way suggested.

PART III

THE NON-METALS

THE NON-METALS

§220. Hydrogen (Gr. *hydro genes* = water forming). H = 1.0078. Atomic No. 1. Valence 1. Discovered by Cavendish in 1766.

1. Physical Properties. — Hydrogen is an odorless, tasteless gas. It is the lightest known substance. Density of the gas, $0.089873 \pm 0.0_527$ under standard conditions of temperature and pressure;[1] of the liquid at $-252°$, 0.070; melting point, $-259.1°$; boiling point, $-252.78° \pm 0.02°$[2] at 760 mm. The critical temperature (T_k) is $-239.91°$;[3] the critical pressure, 12.80 atmospheres.[4] Hydrogen diffuses through walls of paper, porcelain, heated platinum, nickel, iron and other metals more rapidly than any other gas. Many metals occlude or dissolve hydrogen to a remarkable extent, e.g., palladium under suitable conditions will hold 900 times its own volume. This occluded gas acts as a strong reducing agent and is also employed for the hydrogenation of oils (cotton seed, fish, corn, etc.). Hydrogen is a better conductor of heat and sound than air, but is inferior to the metals in that respect. Its refractive index is greater than that of any other gas, and is about six times that of air. It burns with a non-luminous flame and the evolution of much heat. Its chief commercial uses are for the hydrogenation of oils, the preparation of synthetic ammonia, methanol, etc., and for the oxy-hydrogen flame employed in cutting or welding metals.

2. Occurrence. — Hydrogen is occasionally found in volcanic gases, but only a trace is to be found in the atmosphere. It occurs chiefly in combination, as H_2O, and among the elements forms approximately 1% of the earth's crust.

3. Preparation.[5] — (*a*) By the action of superheated steam upon heated metals or glowing coals. (*b*) By the action of dilute acids (seldom HNO_3) on many metals. (*c*) By the electrolysis of aqueous solutions. In the electrolytic preparation of NaOH from salt brine, hydrogen is obtained as a by-product at the cathode. (*d*) In the laboratory, probably the method most extensively used involves the action of dilute H_2SO_4 on metallic Zn. To secure a smooth, even flow of the gas, "platinized" zinc or an alloy containing 10% Cu should be used. The addition of a small amount of $CuSO_4$ to the reaction mixture is also satisfactory.

5. Solubility. — Water at ordinary temperatures dissolves nearly 2% by volume of hydrogen.

6. Reactions. — Hydrogen gas is an indifferent substance at ordinary temperatures. It is occluded or adsorbed by Pd, Pt, Fe, Ni, etc., and is thereby "activated." In such a condition it readily combines with many substances toward which in the ordinary state

[1] Morley, *Smithsonian Contrib.*, No. 980 (1895); *Z. physik. Ch.*, **20**, 271 (1896); cf. Gmelin, 8th ed., No. 2, p. 81.

[2] Henning and Heuse, *Z. Physik*, **23**, 105 (1924).

[3] Kamerlingh, *et al.*, *Koninkl. Akad. Wetenschappen Amsterdam*, **26**, 124 (1917).

[4] *Ibid.*

[5] Cf. Bronn, *Ch. Ztg.*, **50**, 922 (1926); von Skopnik, *Ibid.*, p. 473; Taylor, *Ch. Met. Eng.*, **27**, 1263 (1922).

it is entirely inert. It reacts either directly or indirectly with most of the non-metals and many of the metals to form hydrides[1] (LiH, BH_3, NH_3, H_2O, HCl, etc.). "Nascent" hydrogen (literally, new born) is a powerful reducing agent. Under proper conditions it combines with O, S, Se, Te, Cl, Br, I, N, P, As, Sb and Si with comparative readiness.[2] It should be noted, however, that "nascent" hydrogen generated by different methods does not possess the same reducing properties. Sodium amalgam with acids does not give hydrogen capable of reducing silver halides; the reaction is rapid when Zn° and acids are used. Neither electrolytic hydrogen nor that from sodium amalgam and acids reduces chlorates, while Zn° and acids give rapid reduction to chlorides. Hydrogen obtained from Al° and a fixed alkali does not reduce As^{+5}; that formed by Zn° and acids gives AsH_3; Sb^{+5} with sodium amalgam and acids gives Sb°; with Zn° and acids, SbH_3.[3]

Hydrogen occluded by metals also forms a very powerful reductant. Hydrogen adsorbed by Pd° precipitates Ag, Au, Pt, Pd, Cu and Hg from their solutions; MnO_4^- in acid solution is reduced to Mn^{++}, Fe^{+3} to Fe^{++}; and Cr^{+6} to Cr^{+3}. The reactions are quantitative. Salts of Pb, Bi, Cd, As, Sb, W, Mo, Zn, Co, Ni, Al, Ce, U, Rb, Cs, K, Na, Ba, Sr and Ca are not reduced. In the presence of platinum black $K_3Fe(CN)_6$ is reduced to $K_4Fe(CN)_6$; dilute HNO_3 to NH_4NO_2; concentrated HNO_3 to HNO_2; Cl, Br and I combine with hydrogen in the dark; ClO_3^- and ClO^- become Cl^-; ClO_4^- is not reduced.

Free hydrogen *very* slowly acts upon a neutral solution of $AgNO_3$, precipitating traces of Ag°; in a concentrated solution $AgNO_2$ is formed. Solutions of Au, Pt and Cu are also acted upon. $KMnO_4$ in acid, neutral or alkaline solution slowly oxidizes hydrogen; aqua regia in diffused daylight does not affect it. The same is true of $FeCl_3$, $K_3Fe(CN)_6$, HNO_3 or H_2SO_4 at room temperatures.

7. **Ignition.** — Chlorine and bromine combine with hydrogen directly in the sunlight, but heat is required to effect combination with iodine, fluorine and oxygen.

All oxides, hydroxides, nitrates, carbonates, oxalates and organic salts of the following elements are reduced to the metallic or elemental state by ignition in hydrogen gas: Pb, Ag, Hg, Sn, Sb, As, Bi, Cu, Cd, Pd, Mo, Ru, Os, Rh, Ir, Te, Se, W, Fe, Cr, Co, Ni, Zn, Tl, Nb, In, V. Compounds of Al, Mn, and of Group V and VI metals have not been reduced to the metallic state by hydrogen.

8. **Detection.** — Hydrogen is detected by (*a*) its explosive union with oxygen when ignited, (*b*) its adsorption on Pd° sponge, (*c*) its explosive union with chlorine in the sunlight to form HCl.

9. **Determination.** — Hydrogen may be most easily determined by combustion to H_2O and weighing as such, or measuring the contraction in volume of the gas sample due to the reaction. It may also be estimated by volume measurement after the removal of other gases.

[1] For an extensive bibliography see: Hüttig, *Z. angew. Ch.*, **39**, 67 (1926).

[2] With a number of these elements the reaction may take place with explosive violence. A mixture of eight parts by weight of oxygen with one part of hydrogen is especially dangerous.

[3] It is believed by many workers that the reactions mentioned above are due to the metal rather than to "nascent" hydrogen.

§221. Boron (and Boric Acid) (Arabian *būraq* = white). B = 10.82. Atomic No. 5. Valence 3. Discovered by Davy in 1808.

1. Physical Properties. — Density 2.3;[1] melting point, 2400°.[2] Boron sublimes at a temperature appreciably below its melting point. Metallic boron has been prepared in two forms: crystalline and amorphous, both probably impure. The latter form is greenish brown, odorless and tasteless. It is a poor conductor of electricity, decidedly infusible and, like tantalum, combines directly with nitrogen of the air when heated. Although some alloys[3] have been prepared, there are practically no commercial uses for the metal. Boric acid and borates (principally sodium and calcium) are used in the manufacture of enamel coatings for bath tubs, kitchen ware, etc.; for making glass, e.g., "pyrex"; for pottery glazes; as a flux in assaying, soldering and welding metals; as a mild disinfectant; as a water softener in laundries; and for cleaning hides in the tanning industry.

2. Occurrence. — Boron, in the form of its various minerals, is widely scattered in small deposits. It occurs chiefly as boric acid, H_3BO_3, and borates: colemanite, $Ca_2B_6O_{11} \cdot 5H_2O$; datolite, $Ca(B \cdot OH)SiO_4$; tourmaline, $H_{20}B_2Si_4O_{21}$; and rasorite (or kernite), $Na_2B_4O_7 \cdot 4H_2O$. Boric acid is obtained chiefly from Italy (cf. 3). The United States, however — particularly California — produces more than half of the world's supply of boron compounds. There, at present, rasorite accounts for about two-thirds of the production, while Searles Lake furnishes almost all of the balance.[4] Borates are also obtained from Chile, Turkey, Italy (see above), Tibet, etc. In 1930 the production of crude borate minerals was slightly less than 180,000 tons valued at 5.3 million dollars. At the same time boric acid was quoted at 5¢–6¢, and borax at $2\frac{3}{4}$¢ per pound.

3. Preparation. — Metallic boron may be prepared by the action of potassium on boric acid. *Boric acid* is obtained by concentration of the water from certain fumaroles in central Italy;[5] also by treating a hot solution of borax with H_2SO_4. Upon cooling, boric acid crystallizes out in a fairly pure state. *Borax*, $Na_2B_4O_7 \cdot 10H_2O$, is readily obtained from rasorite by removal of the gangue and crystallization of the crude product from water to purify it and produce the form commercially demanded. Borax is also secured as a by-product in the recovery of potash at Searles Lake. Up to 1926, when the extensive deposits of rasorite were first exploited, practically all of the borax was made by treating colemanite with sodium carbonate or sulfate and, after removal of the precipitated $CaCO_3$ (or $CaSO_4$), evaporating the filtrate to crystallize the borax.

4. Hydrides, Oxide and Acids. — The hydrides of boron are unimportant analytically.[6] Various oxides have been reported, but apparently only boron trioxide, B_2O_3, is well established. It is obtained by heating H_3BO_3 to complete removal of H_2O. The molten mass is then quickly

[1] Warth, *Bull. Maryland Acad. Sci.*, **3**, 8 (1923).
[2] Guertler and Pirani, *Z. Metallkunde*, **11**, 1–7 (1919).
[3] It is claimed that 1%–2% B is very beneficial in steel.
[4] Cf. *I. C.* 6499 (1931).
[5] A good description of the process may be found in Mellor, V, 49.
[6] For a description of the various hydrides of boron, see: Mellor, V, 33–9; Gmelin, 8th ed., No. 13, p. 54–64.

cooled. It forms a hard, colorless glass that is very brittle; is odorless and has a slightly bitter taste. This oxide reacts with water to form, first HBO_2, then H_3BO_3.[1] Three acids of boron have been prepared in the solid state: orthoboric acid, H_3BO_3[2] or $B_2O_3{\cdot}3H_2O$; tetra- or pyro-boric acid, $H_2B_4O_7$ or $2B_2O_3{\cdot}H_2O$; and metaboric acid, HBO_2 or $B_2O_3{\cdot}H_2O$. They are all white and nicely crystalline.[3] Perboric acid,[4] HBO_3, and a number of heteropolyboric acids have also[5] been described.

5. Solubility. — Boron is practically insoluble in water and solutions of the fixed alkalis; soluble in concentrated HNO_3; attacked by hot H_2SO_4. Boric oxide slowly dissolves in H_2O with formation of H_3BO_3.[6] It is also soluble in dilute HF and in warm, concentrated H_2SO_4. Orthoboric acid dissolves in H_2O at 21°[7] to the extent of 5.14 g./100 g. of the solvent. The solubility is lowered by the presence of many other acids, as HCl, HNO_3, H_2SO_4, etc.; also by some salts, e.g., NaCl, while others have an opposite effect, e.g., KCl, KNO_3, $NaNO_3$, Na_2SO_4, etc. Both tetra- and meta-boric acids form $H_2BO_3^-$ or BO_2^- on treatment with excess H_2O (see above). In general the borates are slightly to moderately soluble in water and acid solutions. The solubility of $Na_2B_4O_7{\cdot}10H_2O$ is 3.9 g./100 g. of H_2O at 35°; of $K_2B_4O_7{\cdot}5H_2O$, 26.7 g./100 g. of H_2O at 30°; the corresponding Li salt is very soluble. The borates of the alkaline earth metals are soluble in H_2O or acid solutions, insoluble in NH_4OH.

6. Reactions. — Boric acid, added to a neutral or slightly acid solution of the common metals, does not give a precipitate. Borax, $Na_2B_4O_7{\cdot}10H_2O$, added to a neutral solution of most of the common metals, gives a precipitate. Apparently no systematic study of the products has been made, but in general they depend upon conditions, particularly those affecting hydrolysis.[8] Silver forms $AgBO_2$[9] contaminated with some Ag_2O; Pb^{++} gives a white precipitate of lead borate;[10] Hg^{++} forms the oxide; Cu^{++} gives a pale blue precipitate; Fe^{+3}, Cr^{+3} and Al^{+3} give precipitates of the corresponding hydroxides; Ba^{++}, Sr^{++} and Ca^{++} in sufficiently concentrated solutions form a white precipitate of $Ba(BO_2)_2$, $Sr(BO_2)_2$ and $Ca(BO_2)_2$

[1] For the action of B_2O_3 with various metal oxides, see: **7**; also Guertler, *Z. anorg. allgem. Ch.*, **40**, 225, 337 (1904).

[2] This is the commercial "boric acid."

[3] Holt (*C.A.* **5**, 3019), has found by the freezing point method that only H_3BO_3 exists in solution.

[4] Pissarjewsky, *Z. physik. Ch.*, **43**, 170 (1903).

[5] Cf. Gmelin, 8th ed., No. 13, p. 94 *et seq.*

[6] Myers, *J. Ch. Soc.*, **111**, 178 (1917).

[7] While H_3BO_3 is readily soluble at temperatures nearer the boiling point of water there is an appreciable loss of the acid at 80° and above due to its volatility. Bauchi and Giannotti, *Ann. ch. applicata*, **20**, 271–85 (1930), *C.A.* **24**, 5596.

[8] Vanino, *Z. anal. Ch.*, **54**, 408–9 (1915), *C.A.* **9**, 3186. Cf. Menzel, *Z. physik. Ch.*, **100**, 276–315 (1922), *C.A.* **16**, 2056.

[9] Abegg and Cox, *Z. physik. Ch.*, **46**, 6 (1903).

[10] Brown and Partington, *J. Soc. Ch. Ind.*, **44**, 325T (1925).

respectively. In ammoniacal solution no precipitate is obtained with ions of Zn, Co or Ni; Ba^{++}, Sr^{++}, Ca^{++} and Mg^{++} give bulky white precipitates which of course would interfere with the analysis of Group III if any large amount of borate were not removed from the Group II filtrate.

Borates are transposed with formation of boric acid, by all ordinary acids — under some conditions even by carbonic acid. The liberated boric acid may be treated with alcohol, forming ethyl borate, which when ignited burns with a green flame. A solution of a borate, acidified with HCl to a barely perceptible acid reaction, imparts to a piece of turmeric paper a dark red color which becomes a characteristic red on drying the paper.

7. **Ignition.** — Boric acid is displaced from its salts by nearly all acids including carbonic; but being readily converted to B_2O_3, which is non-volatile except at a high temperature, it displaces most other acids upon ignition.

A mixture of borax, $KHSO_4$, and a fluoride heated in the Bunsen flame imparts an evanescent yellow-green color to the flame. Borates fused in the inner blowpipe flame with $KHSO_4$ give a green color to the outer flame. If a crystal of boric acid (or a borate residue) is moistened with H_2SO_4 and heated on a platinum wire to expel the excess acid, then dipped in glycerine and burned, the green flame appears with great distinctness. The glycerine is only ignited, then allowed to burn by itself. Barium does not interfere, being converted to the non-volatile sulfate; copper, however, must be removed.

TABLE 39

COLOR OF BORAX BEADS CONTAINING VARIOUS METALS*

Metal	Oxidizing Flame	Reducing Flame
Cu	blue (cold), green (hot)	red
Fe	yellow	green
Cr	green (cold), yellowish (hot)	green
Ti	colorless	violet
Mn	purple	colorless
Co	blue	blue
Ni	brown (cold), reddish (hot)	gray to colorless

* See especially Bancroft and Nugent, *J. Phys. Ch.*, **33**, 481–97 (1929). Cf. §309.

Borax, $Na_2B_4O_7{\cdot}10H_2O$, when ignited (as on a loop of platinum wire to give a borax bead) with many metallic compounds, forms a colored bead that may be used for the detection of certain metals. Details may be found under the individual metals.[1] Table 39 gives a summary of the more important tests.

[1] For a systematic study of the fusion of B_2O_3 with oxides of the metals see: Guertler, *Z. anorg. allgem. Ch.*, **40**, 225 (1904). Cf. Mellor, V, 45.

8. Detection. — Borates are detected by first removing Cu^{++} then adding H_2SO_4 and alcohol[1] or glycerine to the filtrate and burning.[2] The appearance of a green flame is a delicate test for borate. Tumeric paper dipped in a faintly acid solution of borate turns red. Drying the paper intensifies the color.[3] Ammonia turns it blue. Traces of boron may be detected by means of tincture of mimosa blossoms.[4, 5]

9. Determination. — Boron may be separated by conversion to boric acid and addition of methanol followed by volatilization of the methyl borate, $B(OCH_3)_3$, thus formed. The ester is collected in NaOH, saponified, the alcohol removed, and the boric acid titrated with standardized NaOH in the presence of mannite or glycerine, using phenolphthalein as an indicator.[6] Boric acid can also be titrated with accuracy potentiometrically.[7]

10. Oxidation and Reduction. — Boric acid treated with H_2O_2 is said to give perboric acid, HBO_3. The sodium salt,[8] although only slightly soluble in H_2O, is a powerful oxidizing agent. In general its reactions are the same as those of H_2O_2.[9]

§222. Carbon (and its Oxides) (L. *carbo* = charcoal). C = 12.000. Atomic No. 6. Valence (2, 3), 4. Discovery prehistoric.

1. Physical Properties. — Carbon exists in three allotropic forms: two crystalline (diamond and graphite) and one amorphous[10] (coal, coke, etc.). The *densities* of these forms are: diamond, 3.49 ± 0.01;[11] graphite, 2.26;[12] amorphous (charcoal), about

[1] For a modification of the alcohol flame test to detect 0.2 mg. H_3BO_3, see: Gabriel-Tanner, *J. Am. Ch. Soc.*, **50**, 1385 (1928).

[2] This test can be made to detect 0.01 mg. of boric acid. In addition to Cu the following may interfere with the alcohol test: Tl, TeO_2, MoO_3, H_3PO_4. Cf. Lenher and Wells, *J. Am. Ch. Soc.*, **21**, 417 (1899); Krauss, *Ch. Ztg.*, **51**, 38 (1927).

[3] Lavalle, *Ch. Ztg.*, **32**, 816–17 (1908), *C.A.* **2**, 3115, discusses the preparation of a test paper sensitive to one part in 4000. Cf. Chamot and Cole, *Ind. Eng. Ch.*, **10**, 48 (1918), for a very delicate procedure; also Bertrand and Agulhon, *Compt. rend.*, **157**, 1433 (1913).

[4] Robin, *Bull. soc. ch.*, [4] **13**, 602 (1913); cf. *C.A.* **6**, 3244.

[5] Cf. Hillebrand and Lundell, p. 607–8, also Gutzeit, *Helv. Ch. Acta*, **12**, 713–40 (1929), *C.A.* **23**, 4645; Dodd, *Analyst*, **54**, 282–5 (1929), *C.A.* **23**, 4645.

[6] For details see: Hillebrand and Lundell, p. 611 *et seq.* Cf. Weatherby and Chesny, *Ind. Eng. Ch.*, **18**, 820–1 (1926).

[7] Hildebrand, *J. Am. Ch. Soc.*, **35**, 861 (1913).

[8] For preparation see: Le Blanc and Zellmann, *Z. Elektroch.*, **29**, 183 (1923).

[9] Concerning perborates see: Lenz and Richter, *Z. anal. Ch.*, **50**, 537–44 (1911), *C.A.* **5**, 3549; Rossi, (*C.A.* **11**, 1935); Foerster, *Z. angew. Ch.*, **34**, Aufsatzteil, 354–5 (1921), *C.A.* **15**, 3595.

[10] Cf. Latimer and Hildebrand, p. 212. Graphite and amorphous carbon give the same X-ray pattern.

[11] Roth, *et al.*, *Z. Elektroch.*, **31**, 461 (1925).

[12] Ceylon graphite. The value for Acheson graphite is 2.18. Ruff, *et al.*, *Z. anorg. allgem. Ch.*, **148**, 328 (1925).

2.1.[1] Melting point, 3572° ± 45°.[2] Boiling point, about 4000°.[3] Diamond is the hardest substance known. It has a very high index of refraction ($n_D = 2.417$) and its characteristic "fire" is due to the exceptional dispersion (0.058). Ignition in hydrogen does not effect a change; in air or oxygen it burns to CO_2.

Graphite is black, very soft, a good conductor of electricity and a fairly good conductor of heat. It burns with difficulty. It is used in foundry facings, paints, dry cells, lead pencils (mixed with clay to give the desired hardness), for crucibles heated to high temperatures, for electrodes in electric furnaces, etc.

Amorphous carbon is lighter than diamond or graphite. It is used as coal, charcoal, etc. Lampblack is made commercially by burning natural gas (which is chiefly methane, CH_4) with a limited supply of air. It is used as a pigment in paint, in stove-blacking, shoe polish, printers' ink, etc. Charcoal absorbs many gases, hence is valuable in gas masks and as a deodorant.

2. Occurrence. — The principal diamond mines of the world are in South Africa at Kimberley, in the Orange Free State, in the Transvaal — the Premier mine near Pretoria is the largest known — and in the Belgian Congo. This region furnishes over 95% of the diamonds mined and incidentally gives Great Britain a monopoly of the industry. Graphite is found chiefly in Ceylon, Madagascar, Chosen (Korea), Czechoslovakia, Mexico and the United States (principally Alabama, Michigan, Nevada, Rhode Island and Texas).[4] The total world production in 1929 was about 153,000 metric tons. Amorphous carbon occurs in many parts of the world chiefly as a decomposition product of organic material, air being excluded, e.g., anthracite and bituminous coal.

Carbon in combination as vegetable and animal tissue, carbonate rocks, petroleum, natural gas, carbon dioxide, etc., is widely distributed but the element ranks only eleventh in abundance.

3. Preparation. — Very small diamonds have been prepared by saturating iron with carbon at 3000° then quickly chilling the exterior of the mass in order to create as high a pressure as possible in the interior.[5] Naturally occurring diamonds are believed to have been crystallized from molten magnesium silicates far beneath the surface of the earth where the pressure is very high. Any form of carbon volatilizes when heated to about 3500°; upon cooling, the vapor condenses to form graphite. Artificial graphite is manufactured in large quantities from anthracite coal or petroleum coke (at Niagara Falls). Pure amorphous carbon may be prepared by ignition of cane sugar.[6]

4. Hydrides, Oxides and Acids. — Carbon forms many hydrides or hydrocarbons, only one of which will be mentioned here. Methane, CH_4, marsh gas, is colorless and odorless. It is the chief component of natural gas, that from some sources being practically pure. It is used for heating, lighting and the manufacture of lampblack.

[1] Howard and Hulett, *J. Phys. Ch.*, **28**, 1095 (1924), show that the value varies widely, depending upon the source of the charcoal.

[2] Ryschkewitsch and Merck, *Z. Elektroch.*, **32**, 42 (1926). Cf. Alterthum, *Z. tech. Physik*, **6**, 540 (1925).

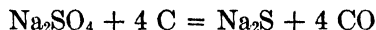
[3] Cf. Kohn and Guckel, *Z. Physik*, **27**, 341 (1925), *C.A.* **19**, 11.

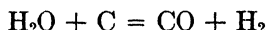
[4] Mineral Ind., **1929**. Texas furnished practically the entire supply of crystalline graphite in 1929.

[5] Moissan, *Compt. rend.*, **118**, 320 (1894).

[6] Bartell and Miller, *J. Am. Ch. Soc.*, **44**, 1866–80 (1922).

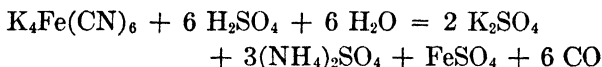
Carbon monoxide,[1] CO, is an odorless, colorless gas; density, 1.250 g./l.[2] at S.T.P.; melting point, − 200°; boiling point, − 190°. It is very toxic when inhaled, combining with the hemoglobin of the blood from which elimination is rather slow even in cases of slight poisoning. Large amounts are usually fatal.[3] Carbon monoxide is readily obtained[4] (1) by the incomplete combustion of coal; (2) by heating Na_2SO_4 with excess of charcoal (Le Blanc's soda process);

$$Na_2SO_4 + 4\ C = Na_2S + 4\ CO$$

(3) by passing steam over charcoal at a white heat (water gas);

$$H_2O + C = CO + H_2$$

(4) by passing CO_2 over red hot charcoal; (5) by heating a formate, oxalate, or ferrocyanide with concentrated H_2SO_4;

$$HCOOH(+\ H_2SO_4) = CO + H_2O^{5}$$

$$Na_2C_2O_4 + H_2SO_4 = Na_2SO_4 + CO + CO_2 + H_2O$$

$$K_4Fe(CN)_6 + 6\ H_2SO_4 + 6\ H_2O = 2\ K_2SO_4 + 3(NH_4)_2SO_4 + FeSO_4 + 6\ CO$$

Carbon monoxide is slightly soluble in H_2O, 3 cc./100 cc. at 8°. It reacts with the alkali hydroxides to form formates ($CO + NaOH = HCOONa$); is absorbed by charcoal and cuprous chloride; forms carbonyls with several of the metals, e.g., $Ni(CO)_4$ and $Fe(CO)_5$.

Carbon monoxide is an energetic reducing agent. In the sunlight it combines directly with Cl_2 or Br_2.[6] It is oxidized to CO_2 by warming with $K_2Cr_2O_7$ and H_2SO_4, by iodine pentoxide[7] ($5\ CO + I_2O_5 = 5\ CO_2 + I_2$), also by $PdCl_2$ which is reduced to Pd° (cf. p. 286, 6).[8] It may be detected by combustion to CO_2 (q. v.) and detected as such, or in the blood, by examination of the absorption spectrum. The latter is the principal method in toxicological work.

Carbon dioxide, CO_2, carbonic anhydride, is an odorless, tasteless and

[1] The various suboxides are not of present importance.
[2] Pire and Moles, *Anales soc. españ. fís. quím.*, **27**, 267–72 (1929), *C.A.* **23**, 4382.
[3] 1% in the air breathed will cause death in a few minutes.
[4] Cf. Thompson, *Ind. Eng. Ch.*, **21**, 389–94 (1929), for preparation of CO 99.9% pure.
[5] Cf. Muller and Peytral, *Bull. soc. ch.*, **29**, 34–9 (1921).
[6] See: Piva, *Gazz. ch. ital.*, **45**, I, 219 (1915).
[7] This reagent is used for the determination of CO in gas analysis.
[8] Cf. Desgrez and Labat, *Ann. ch. anal. ch. appl.*, **24**, 294-5 (1919), *C.A.* **14**, 712; Nowicki, *Ch. Ztg.*, **35**, 1120 (1911), *C.A.* **6**, 1. For the action of CO with halogen compounds of Ir, Os, Rh and Ru see: Manchot, *et al.*, *Ber.*, **57B**, 2130 (1924), **58B**, 229, 232, 2173 (1925).

colorless gas; density, 1.97686 g./l.;[1] melting point, – 56.6°[2] (at 1 atmosphere pressure); critical temperature, 31.35°; critical pressure, 73 atmospheres. This gas is non-toxic, but it will produce death by suffocation. Carbon dioxide is readily obtained (1) by the combustion of carbon or CO with excess of oxygen; (2) by the interaction of an acid and a carbonate ($CaCO_3 + 2\ HCl = CaCl_2 + CO_2 + H_2O$); (3) as a by-product of various fermentation industries; (4) from certain wells in Mexico and the United States. The solubility of CO_2 in water is 0.145 g./100 cc. H_2O at 25°. Combination with this solvent produces the hypothetical H_2CO_3[3] which reacts acid to litmus. The gas is rapidly absorbed by hydroxides of the alkalis and of the alkaline earths, forming normal or acid carbonates: $2\ NaOH + CO_2 = Na_2CO_3 + H_2O$, $NaOH + CO_2 = NaHCO_3$. The carbonates of the alkalis are soluble in H_2O [the acid (or bi-) carbonates are less soluble than the normal salts], other carbonates are insoluble to slightly soluble.[4] The presence of some other salts, especially ammonium salts, prevents the precipitation of some carbonates, notably magnesium carbonate (p. 415, 6 *a*). Many of the carbonates are soluble in H_2O saturated with CO_2, forming acid carbonates. Boiling removes the excess CO_2, thus causing precipitation of the carbonate.

The chief commercial uses for carbon dioxide are for carbonated beverages, refrigeration ("Dry-Ice"), fire extinguishers and the manufacture of sodium carbonates (baking and washing soda).

6. **Reactions.** — (1) *Carbon.* The important reactions of this element take place chiefly at higher temperatures. They are described below (**7**). (2) *Carbon Monoxide* (see p. 446). (3) *Carbon Dioxide and Carbonates.* Carbonates of the fixed alkalis precipitate from solution all other metallic cations;[5] with Sb the precipitate is an oxide; with Sn, Al, Cr and Fe^{+3} it is an hydroxide; with Ag, Hg_2^{++}, Cd, Fe^{++}, Mn^{++}, Ba, Sr and Ca it is a normal carbonate; with other metals a basic carbonate, except that $HgCl_2$ gives a basic chloride. The carbonates of Ag, Hg and Cu decompose more or less readily, especially upon heating, to form the corresponding oxide. Carbonic acid is completely displaced from all carbonates by strong acids, e.g., by HCl, $HClO_3$, $H_2C_2O_4$, HNO_3, H_3PO_4, H_2SO_4, and even by H_2S.[6] The separation is complete from carbonates of the first four groups, incomplete from those of the fifth and sixth groups.

[1] Deshusses, Dissert., 1922.

[2] Bridgeman, *Phys. Rev.*, [2] **3**, 153 (1914).

[3] Cf. Thiel, *Z. anorg. allgem. Ch.*, **121**, 211–4 (1922), *C.A.* **16**, 4154, and references there given.

[4] Seyler and Lloyd, *J. Ch. Soc.*, **111**, 994–1001 (1917). This is their third article on the solubility of carbonates.

[5] For a study of the precipitating power of Na_2CO_3 upon metallic salts under similar conditions see: Wells, *J. Wash. Acad. Sci.*, **1**, 21–4 (1911), *C.A.* **5**, 3206.

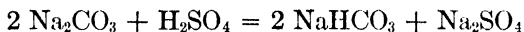
[6] For the action of CO_2 on inorganic sulfides see: Costeanu, *Ann. ch.*, **2**, 189–210 (1914), *C.A.* **9**, 1881.

Ammonium carbonate precipitates from solution all of the non-alkali metals except Mg, chiefly as carbonates. In the case of those metals that form ammines (Ag, Cu, Cd, Co, Ni and Zn) the precipitate dissolves in an excess of the reagent.

The decomposition of carbonates by acids is usually attended by marked effervescence of gaseous CO_2:

$$Na_2CO_3 + H_2SO_4 = Na_2SO_4 + CO_2 + H_2O$$

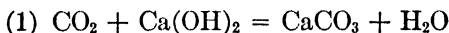
With normal carbonates in cold solution, addition of a small amount of acid (short of saturation of half the base) does not cause effervescence, because an acid carbonate is formed:

$$2\ Na_2CO_3 + H_2SO_4 = 2\ NaHCO_3 + Na_2SO_4$$

When there is much free alkali present (as in testing caustic alkalis for slight admixtures of carbonate) perhaps no effervescence will be obtained, for by the time all of the alkali is neutralized there is enough water present to dissolve the small amount of gas liberated. If, however, the carbonate solution is added to the acid dropwise, so that the latter is constantly in excess, a fairly small amount of carbonate will give a perceptible effervescence.

The effervescence of CO_2 is distinguished from that of H_2S or SO_2 by the lack of odor, from that of hydrogen by the difference in rate of evolution and the fact that CO_2 will not burn. It should be noted that CO_2 is evolved (with CO) upon adding concentrated H_2SO_4 to oxalates or to cyanates.

When CO_2 is passed into a solution of $Ca(OH)_2$, $Ba(OH)_2$ (Eq. 1), $CaCl_2$, $BaCl_2$ (Eq. 2) (the latter two containing excess NH_4OH) or into an ammoniacal solution of lead acetate, a white precipitate or turbidity of the corresponding carbonate is formed.

$$(1)\ CO_2 + Ca(OH)_2 = CaCO_3 + H_2O$$

$$(2)\ CO_2 + BaCl_2 + 2\ NH_4OH = BaCO_3 + 2\ NH_4Cl + H_2O$$

The solutions of $Ca(OH)_2$ and $Ba(OH)_2$ furnish more delicate tests for CO_2 than the ammoniacal solutions of $CaCl_2$ and $BaCl_2$ but less delicate than the basic lead acetate solution. The latter is so quickly affected by atmospheric CO_2 that it cannot be preserved in bottles partly full and frequently opened, nor can it be diluted except with recently boiled water. Carbonates of the alkaline earth metals are readily converted to soluble acid carbonates by an excess of CO_2, hence the disappearance of the $CaCO_3$ or $BaCO_3$ precipitate in the tests described above is evidence of an excess CO_2, not of its absence. Solutions thus obtained will effervesce on heating, with escape of CO_2 and reprecipitation of the normal carbonate:

$$Ca(HCO_3)_2 = CaCO_3 + H_2O + CO_2$$

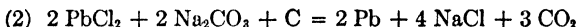
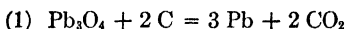
7. Ignition. — *a. Carbon.* — When ignited in air or oxygen, carbon slowly burns to CO_2. If moisture has been carefully excluded previously the action is very slow, especially in the case of graphite. When ignited in an atmosphere of CO_2 both forms of carbon become CO: $C + CO_2 = 2\,CO$. By fusion with $NaNO_3$ or a chlorate, carbon is oxidized to CO_2.

Simple ignition with carbon reduces all oxides of elements in the following list to the metal (Eq. 1). If Na_2CO_3 is also added all salts of these elements are likewise reduced (Eq. 2): Ag, Pb, Hg, Cu, Bi, Cd, As, Sb, Sn, Pd, Mo, Ru, Os, Rh, Ir, Te, Se, W, K, Na, Rb, Cr, Fe, Mn, Co, Ni, Zn, Ti, Tl. With an excess of carbon CO is formed (Eq. 3) while an excess of the oxide gives CO_2 (Eq. 4). (In the reduction of iron ore, the process is conducted so as to give both CO and CO_2.) To obtain certain of the metals in the free state (such as K and Na), special methods are required to exclude the air and produce the high temperature needed.

(1) $Pb_3O_4 + 2\,C = 3\,Pb + 2\,CO_2$

(2) $2\,PbCl_2 + 2\,Na_2CO_3 + C = 2\,Pb + 4\,NaCl + 3\,CO_2$

(3) $CuO + C\ (\text{excess}) = Cu + CO$

(4) $2\,CuO + C = 2\,Cu + CO_2$

All compounds of sulfur, when ignited with carbon, are reduced to the sulfide: $BaSO_4 + 2\,C = BaS + 2\,CO_2$. *b. Carbon monoxide.* When a metallic oxide is ignited in an atmosphere of CO, reduction to the metal takes place as when ignited with carbon. The various metal carbonyls are decomposed into the metal and CO when heated to a sufficiently high temperature (see: the Mond process for Ni). *c. Carbonates.* Normal carbonates of the fixed alkalis are not decomposed upon ignition. The carbonates of the alkaline earth metals are rapidly converted to the oxide at about the following temperatures: $MgCO_3$, 500°;[1] $CaCO_3$, 900°; $SrCO_3$, 1200°; $BaCO_3$, 1350°.[2] In general, at lower temperatures, ignition changes all other carbonates to the oxide and CO_2, except that the carbonates of Ag, Hg and some of the rarer elements are reduced to the metal, CO_2 and O_2 being evolved. Stannous and ferrous oxides, ignited in an atmosphere of CO_2, are changed to SnO_2 and Fe_2O_3, respectively, with evolution of CO.

8. Detection. — *a. Carbon* is detected by its appearance, by its failure to react with general reagents, and by its combustion to CO_2 with air or with $K_2Cr_2O_7$ and concentrated H_2SO_4, the gas being identified by means of $Ba(OH)_2$[3, 4]. *b. Carbon monoxide* is detected by its reduction of $PdCl_2$ to Pd° [which may be detected with MoO_4^{--} (p. 286, 6)]; by its liberation of I_2 from I_2O_5 or HIO_3; by its absorption spectrum when in combination with the hemoglobin of the blood. *c. Carbonates* are detected: by the effervescence when treated with dilute acids;[5] by the precipitate that CO_2 forms with solutions of $Ca(OH)_2$,[6] $Ba(OH)_2$ or lead acetate. The detection

[1] Cf. Mellor, IV, 352.

[2] Cf. Mellor, III, 654–5; also Johnston, *J. Am. Ch. Soc.*, **30**, 1357–65 (1908).

[3] Mixter and Haigh, *J. Am. Ch. Soc.*, **39**, 374 (1917), give a satisfactory method for the detection of C in minerals, depending upon the ignition of the sample with $PbCrO_4$ and action of the CO_2 on $Ba(OH)_2$.

[4] Müller, *J. prakt. Ch.*, **95**, ii, 53 (1917), has suggested heating the sample with potassium azide to obtain KCN which is easily recognized by means of the Prussian blue test.

[5] This test is satisfactory only for CO_3^{--} in large amount, due to the solubility of CO_2 in H_2O.

[6] For the detection of traces of CO_2 see: Rae, *Pharm. J.*, **121**, 315 (1928), *C.A.* **23**, 579.

of carbonate in a bicarbonate may be effected by adding $CaSO_4$ to a 5% $NaHCO_3$ solution. A marked turbidity is obtained with 4% CO_3^{--}.[1] Carbonate may also be detected in an acid carbonate solution by the reaction with phenolphthalein which turns pink if CO_3^{--} is present.[2] For the detection of an acid carbonate in a carbonate, Haslam[3] suggests precipitation of the CO_3^{--} with Ca^{++} and addition of NH_4OH to the filtrate. He states that a precipitate of $CaCO_3$ is produced if one part of HCO_3^- in 1000 is present, although the separation is slow with the lower concentrations.

9. Determination. — *a. Carbon,* in steel or other materials, may be determined by combustion to CO_2 and absorption of the purified and dried gas in KOH or "ascarite,"[4] any increase in weight being due to the CO_2; or the gas may be absorbed in $Ba(OH)_2$ and the excess alkali determined by titration with HCl using phenolphthalein as an indicator.[5] *b. Carbon monoxide* may be determined by ignition to CO_2, the subsequent procedure being that outlined above, or by absorption of the CO in cuprous chloride with measurement of the change in gas volume. *c. Carbonates* may be determined by weighing as such, e.g., $CaCO_3$ (p. 408, 9); or by liberation of the CO_2 which may be measured or absorbed as indicated above.

10. Oxidation and Reduction. — *Carbon* at higher temperatures is one of the most powerful reducing agents known. Either alone or in combination with Na_2CO_3 it will reduce compounds of practically all other metals to the metallic state (see p. 449). The carbon itself may become CO or CO_2, depending upon conditions. *Carbon monoxide* usually acts as a powerful reducing agent (see above). *Carbon dioxide,* except at higher temperatures, does not act as an oxidizing agent.[6]

[1] Macri, *Boll. ch. farm.*, **63**, 531–3 (1924), *C.A.* **19**, 1831. Kolthoff, *Pharm. Weekblad,* **54**, 1046 (1917), *C.A.* **11**, 3194, believes that the precipitation tests are not sensitive enough.

[2] Cf. Macri, *Ibid.*; Kolthoff, *Ibid.*; Sabalitschka and Kubisch (*C.A.* **18**, 2788).

[3] Haslam, *Boll. ch. farm.*, **53**, 271–2 (1914), *C.A.* **9**, 1886; *J. Am. Ch. Soc.*, **34**, 822–3 (1912).

[4] Ascarite is asbestos impregnated with NaOH.

[5] The details of these methods, as regards steel especially, have been worked out to give very accurate results in a minimum of time. For particulars see any of the manuals on steel analysis, such as Lundell, Hoffman and Bright, "Chemical Analysis of Iron and Steel," New York, John Wiley & Sons, Inc. (**1931**), Chapter IX.

[6] Concerning the percarbonates see: Tanatar, *Ber.*, **43**, 127–8 (1910), *C.A.* **4**, 999; Riesenfeld and Reinhold, *Ibid.*, **42**, 4377–83 (1909), *C.A.* **4**, 724; Wolffenstein and Peltner, *Ibid.*, **41**, 280–97 (1908), *C.A.* **2**, 1532.

§223. Acetic Acid. $HC_2H_3O_2$

```
     H   O
     |   ||
 H - C - C - O - H
     |
     H
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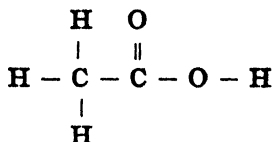
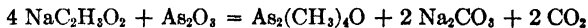

1. Physical Properties. — Pure (glacial) acetic acid is a colorless, crystalline, hygroscopic solid, melting at 16.60°,[1] and boiling at 118.1°. Its density is 1.051 at 20°. It has a sharp, sour taste, an irritating, burning effect on the skin, and a very penetrating odor. It is inflammable near the boiling point, and vaporizes from its concentrated solutions at room temperature with the characteristic odor of vinegar (which is essentially a 4%–5% solution of acetic acid). It is a weak, monobasic acid, three of the hydrogen atoms (linked directly to carbon) not being replaceable by metals.

3. Preparation. — (*a*) By the dry distillation of wood. (*b*) By the fermentation of cider, wine, molasses, alcohol, etc. (*c*) Pure acetic acid is prepared by distilling anhydrous sodium acetate with concentrated sulfuric acid.[2]

5. Solubility. — Acetic acid is miscible with water in all proportions. The salts of acetic acid, acetates, are all readily soluble in water except that silver and mercurous acetates are sparingly soluble. Certain *basic* acetates, as Fe^{+3}, Al^{+3}, etc., are insoluble in water. Many of the acetates are soluble in alcohol.

6. Reactions.[3] — The stronger mineral acids transpose the acetates, forming acetic acid. Anhydrous acetates, with concentrated H_2SO_4, give pure acetic acid (cf. 4), but if the H_2SO_4 is in excess and heat is applied, the mixture will blacken with separation of carbon; at higher temperatures CO_2 and SO_2 will be evolved. If acetic acid or an acetate is warmed with H_2SO_4 and a small amount of an alcohol, the characteristic pungent and fragrant odor of the corresponding ester is obtained.[4]

7. Ignition. — By ignition alone, acetates blacken, with evolution of acetone, CH_3COCH_3, which is inflammable, and agreeable in odor. Prolonged ignition of acetates in air produces carbonates free from charcoal. Ignition with alkali hydroxides yields methane. Heating with an alkali and arsenious oxide forms the offensive and very poisonous vapor of cacodyl oxide. This test should be made under a good hood with great caution, using small quantities of the reagents. It is a very delicate test for acetates:

$$4\ NaC_2H_3O_2 + As_2O_3 = As_2(CH_3)_4O + 2\ Na_2CO_3 + 2\ CO_2$$

[1] Bousfield and Lowry, *J. Ch. Soc.*, **99**, 1436 (1911).

[2] Cf. Beilstein, 4th ed., II, 98; Suppl. II, 41.

[3] Cf. 6 *b*, under the individual metals. In Beilstein, *loc. cit.*, will be found a detailed description of the various acetates.

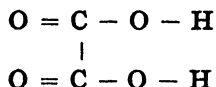
[4] Amyl alcohol is often used because of the well-known banana-like odor of the ester, amyl acetate. It should be noted, however, that both the alcohol and the ester are poisonous.

8. Detection.[1] — Acetic acid is detected (*a*) by its odor; (*b*) by the formation of fragrant ethyl acetate upon warming with H_2SO_4 and alcohol; (*c*) by ignition with As_2O_3 to cacodyl oxide; (*d*) by the development of a blue color when an acetate is treated with $La(NO_3)_3$, iodine and a few drops of NH_4OH. On gradually heating to the boiling point the blue color appears. Homologs of acetic acid, sulfates and any other anion precipitating La^{+3} interfere.[2, 3]

9. Determination. — After separation of other volatile acids by precipitation, H_2SO_4 is added and the acetic acid distilled into H_2O or standardized alkali and the acid or excess alkali is then determined by titration potentiometrically or using phenolphthalein as an indicator.

10. Oxidation and Reduction. — Acetic acid is a very stable organic compound. It is not oxidized by MnO_4^- even in boiling solution. It reduces Au^{+3} only in alkaline solution and does not reduce an alkaline copper solution. Persulfates react with acetates to give CH_4 and CO_2.[4]

§224. Oxalic Acid. $H_2C_2O_4$

$$\begin{array}{c} O = C - O - H \\ | \\ O = C - O - H \end{array}$$

1. Physical Properties. — Anhydrous oxalic acid, $H_2C_2O_4$, is a white, amorphous solid. It may be sublimed at 150° with only partial decomposition: $H_2C_2O_4 = CO_2 + CO + H_2O$. Hydrated oxalic acid, $H_2C_2O_4 \cdot 2H_2O$, effloresces very slowly in warm, dry air, and melts in its water of crystallization at 98°, at which temperature the liquid soon evaporates leaving the anhydrous acid. Oxalic acid is a moderately strong acid, readily displacing weaker acids and, to a certain extent, those stronger, especially if an insoluble oxalate forms with the cation. The acid or a derivative finds application in the manufacture of dyes, in dyeing, in the leather industry, in the preparation of dextrin, and in photography.

2. Occurrence. — It is found in many plants in the free state or as an oxalate. In sorrel it is found as KHC_2O_4, in rhubarb as CaC_2O_4, in lignite deposits as ferrous oxalate, and in guano as ammonium oxalate.

3. Preparation.[5] — (*a*) Sawdust, particularly of the soft woods, is treated with NaOH and then heated, whereupon decomposition takes place, involving the production of an oxalate. This may be extracted with hot H_2O and the precipitate, obtained by evaporation, purified or

[1] Cf. Krüger and Tschirch, *Ch. Ztg.*, **54**, 42–4 (1930), *C.A.* **24**, 1317; Curtman, *et al.*, *Ch. News*, **120**, 230–1 (1920), *C.A.* **14**, 2594, have studied the various tests for an acetate.

[2] Tschirch (*C.A.* **25**, 2665).

[3] The $FeCl_3$ test often suggested for the detection of acetates is not very satisfactory. Cf. Curtman and Harris, *J. Am. Ch. Soc.*, **39**, 1315 (1917).

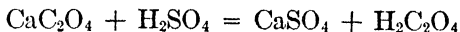
[4] Gordon, *J. Phys. Ch.*, **18**, 55–66 (1914).

[5] Cf. Ullmann, VIII, 218 (1931). Thorpe, IV, 729 (1922).

converted to $H_2C_2O_4$. The latter is accomplished through separation of the oxalate as CaC_2O_4 and removal of the Ca by means of H_2SO_4. (*b*) Oxalic acid may be obtained by the action of HNO_3 (sp. g. 1.38) upon sawdust, starch or sugar. The continued action of concentrated HNO_3, after the sugar is all oxidized to $H_2C_2O_4$ results in the formation of CO_2. (*c*) Sodium formate heated with a variety of substances, as Na_2CO_3, 1% NaOH, crude oxalate, etc., is converted to sodium oxalate.

Oxalates are obtained (*a*) by treating the oxide, hydroxide or carbonate with oxalic acid. In this way the oxalates of Pb, Ag, Hg_2^{++}, Hg^{++}, Sn^{++}, Bi, Cu^{++}, Cd, Zn, Al, Co, Ni, Mn, Fe^{++}, Fe^{+3}, Cr^{+3}, Ba, Sr, Ca, Mg, Na, K and many others are obtained. (*b*) The addition of oxalic acid to a soluble salt of the metal will also yield an oxalate. In this way oxalates of the above metals may be prepared except those of the alkalis, Mg, Cr^{+3}, Fe^{+3}, Al^{+3} and Sn^{+4}, which are not precipitated. Sb^{+3} forms a basic salt. Addition of an excess of $H_2C_2O_4$ may result in the formation of an acid oxalate or a double oxalate. (*c*) Alkali oxalates will precipitate the same ions as oxalic acid, but many of the precipitates are soluble in excess of the reagent with the formation of a double salt, e.g., $AgNH_4C_2O_4$. Ba, Sr and Ca are well defined exceptions to this rule, their precipitates, formed by this method, being normal oxalates. (*d*) Some of the metals, when finely divided, are attacked by $H_2C_2O_4$, hydrogen being evolved. On the other hand, certain metals decompose the reagent, CO_2 being formed (cf. 10).

5. Solubilities. — Anhydrous oxalic acid is hygroscopic; it has been recommended as a drying agent for certain work. Its solubility in H_2O is 9.52 g./100 g. of solvent at 20°.[1] Oxalates of the alkalis, Be and Fe^{+3} are soluble in H_2O [$Na_2C_2O_4$, 3.7 g. and $(NH_4)_2C_2O_4$, 5.3 g. per 100 g. of solvent at 20°]. Nearly all other oxalates are insoluble to slightly soluble. They are readily transposed by the mineral acids:

$$CaC_2O_4 + H_2SO_4 = CaSO_4 + H_2C_2O_4$$

Acetic acid does not dissolve the oxalates, its extent of ionization being distinctly lower than either the primary or secondary ionization of oxalic acid. Certain of the oxalates dissolve appreciably in oxalic acid, due to the formation of acid oxalates.

6. Reactions. — *A. With metals and their compounds.*[2,3] — Oxalic acid and soluble oxalates precipitate from solution most of the metal cations. With excess reagent soluble double oxalates are formed in some cases. An excess of $C_2O_4^{--}$ partially transposes the alkaline earth carbonates, and vice versa, in accord with the Law of Mass Action. In aqueous solution

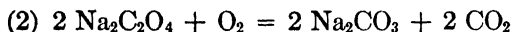
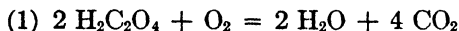
[1] Koppel and Cahn, *Z. anorg. allgem. Ch.*, **60**, 110 (1908).

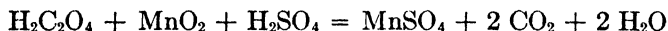
[2] Cf. division 6 *b* under the individual metals.

[3] For a description of the various metal oxalates see especially: Beilstein, 4th ed., II, 502–33; Suppl., II, 217–31.

$H_2C_2O_4$ may release H_2S from FeS and MnS but not from ZnS, CoS or NiS. Oxalic acid is a reducing agent, being converted to water and CO_2 (Eq. 1) by all strong oxidizing agents. Metal oxalates under the same conditions become metal carbonates and CO_2 (Eq. 2).

(1) $2\ H_2C_2O_4 + O_2 = 2\ H_2O + 4\ CO_2$

(2) $2\ Na_2C_2O_4 + O_2 = 2\ Na_2CO_3 + 2\ CO_2$

1. Ag^+ forms a white, crystalline precipitate of silver oxalate in neutral solutions of $C_2O_4^{--}$. The product is explosive when dry.
2. PbO_2 forms lead oxalate and CO_2 with $H_2C_2O_4$.[1] Oxalic acid has no action on Pb_3O_4, but reacts quickly in the presence of any acid capable of changing Pb_3O_4 to PbO_2.
3. Oxalic acid or $(NH_4)_2C_2O_4$ boiled with $HgCl_2$ in the sunlight gives Hg_2Cl_2 and CO_2. In the absence of light a trace of $S_2O_8^{--}$, MnO_2, MnO_4^-, KNO_2 or HNO_3 plus $MnSO_4$ will cause the reaction to take place.[2]
4. $AuCl_3$ is slowly reduced by $H_2C_2O_4$ in the dark, rapidly in sunlight.
5. *Bismuth* having a valence greater than three, forms bismuth oxalate and CO_2.
6. AsO_4^{-3} is reduced to AsO_3^{-3} and CO_2 is evolved.
7. $FeCl_3$ reacts with $H_2C_2O_4$ to give $FeCl_2$ in the sunlight.
8. $Cr_2O_7^{--}$ is reduced to Cr^{+3}. A good catalyst for this reaction is $MnSO_4$.
9. Co_2O_3, $Co(OH)_3$ and NiO_2 are all reduced to the bivalent state with liberation of CO_2.
10. MnO_2 in the presence of H_2SO_4 forms $MnSO_4$ and CO_2:

$$H_2C_2O_4 + MnO_2 + H_2SO_4 = MnSO_4 + 2\ CO_2 + 2\ H_2O$$

MnO_4^- in cold alkaline solution has no action on $C_2O_4^{--}$; in hot acid solution rapid oxidation takes place (cf. 9).

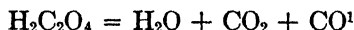
As a rule, reducing agents have no effect on oxalic acid at ordinary temperatures. It is reduced, however, by sodium amalgam and H_2O, Mg° and H_2O, Zn° and H_2SO_4. The initial product is glyoxalic acid, further reduction giving glycollic acid.

B. With non-metals and their compounds.

1. *HCN, HCNS,* $H_4Fe(CN)_6$ and $H_3Fe(CN)_6$ apparently are without action upon $H_2C_2O_4$.
2. HNO_2 catalyzes the oxidation of $H_2C_2O_4$ by $HgCl_2$, otherwise it (HNO_2) seems to be without action. Concentrated HNO_3 decomposes $H_2C_2O_4$ with the formation of CO_2, NO and H_2O.[3]

[1] If 4 parts of anhydrous $H_2C_2O_4$ are mixed with 21 parts of PbO_2 the mass will glow.
[2] Dhar, *J. Ch. Soc.*, **111**, 691, 748, 752 (1917).
[3] Cf. Villiers, *Compt. rend.*, **124**, 1349 (1897).

3. H_3PO_2, H_3PO_3, H_3PO_4 have no action upon $H_2C_2O_4$.
4. Warm, concentrated H_2SO_4 decomposes oxalic acid:

$$H_2C_2O_4 = H_2O + CO_2 + CO$$[1]

Oxalic acid, treated with a *persulfate*, dilute H_2SO_4 and a small amount of Ag^+, is quantitatively converted to CO_2.

5. With *chlorine*, HCl and CO_2 are formed. This reaction takes place more readily in neutral or alkaline solution, forming a chloride and CO_2 if the solution is neutral, CO_3^{--} if alkaline. *HClO* forms Cl_2 and CO_2. If the $H_2C_2O_4$ is in excess HCl is formed. The action is more rapid in a neutral or alkaline medium, a chloride and a carbonate being formed. $HClO_3$ forms CO_2 and varying amounts of Cl_2 and HCl. A high temperature and excess of $H_2C_2O_4$ favors the production of HCl.

6. *Bromine* oxidizes $H_2C_2O_4$ slowly; but reacts readily with soluble oxalates in neutral or alkaline solution, the reactions being similar to those of chlorine. With $HBrO_3$, bromine and CO_2 are formed; with excess of warm $H_2C_2O_4$ hydrobromic acid is formed.

7. HIO_3 reacts with $H_2C_2O_4$ to give CO_2 and I_2. With mixtures of ClO_3^-, BrO_3^- and IO_3^-, the ClO_3^- is first decomposed, then the BrO_3^-[2] and finally the IO_3^-.

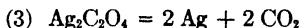
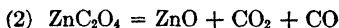
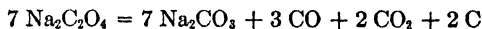
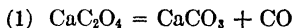
7. Ignition.[3] — When anhydrous $H_2C_2O_4$ is heated it decomposes into CO_2, CO and H_2O.[4] If the acid is mixed with alumina, the reaction takes place at a much lower temperature (ca. 90°).

All oxalates are decomposed upon ignition. Those of the alkali and alkaline earth metals are resolved at a low red heat into carbonate and CO (Eq. 1). The oxalates of metals whose carbonates are easily decomposed, but whose oxides are stable, are changed into oxides, CO_2 and CO (Eq. 2). The oxalates of metals whose oxides are decomposed by heat leave the metal and give off CO_2 (Eq. 3).

(1) $CaC_2O_4 = CaCO_3 + CO$

$7\ Na_2C_2O_4 = 7\ Na_2CO_3 + 3\ CO + 2\ CO_2 + 2\ C$

(2) $ZnC_2O_4 = ZnO + CO_2 + CO$

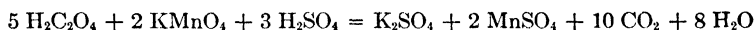
(3) $Ag_2C_2O_4 = 2\ Ag + 2\ CO_2$

If dry NaCl is heated with $H_2C_2O_4 \cdot 2H_2O$ all of the chlorine is expelled as HCl.

8. Detection. — (*a*) The oxalate ion may be detected by precipitation in a neutral, alkaline or acetic acid solution as CaC_2O_4. The precipitate is washed and dissolved in hot, dilute H_2SO_4. If the resulting solution is treated with dilute $KMnO_4$ the first few drops will be reduced very slowly to the colorless Mn^{++}, after which the purple color will disappear rapidly

[1] Lichty, *J. Phys. Ch.*, **11**, 225–72 (1907).
[2] In acid solutions BrO_3^- has practically the same oxidation potential as ClO_3^-.
[3] Herschkowitsch, *Z. anorg. allgem. Ch.*, **115**, 159–67 (1922), *C.A.* **16**, 3789.
[4] Probably some C is also obtained.

until all of the $C_2O_4^{--}$ has been oxidized.[1] (*b*) Warming an oxalate with concentrated H_2SO_4 after decomposition of carbonates with dilute H_2SO_4 results in the liberation of CO_2 and CO. The former may be detected by means of $Ba(OH)_2$ and the latter by its combustibility. (*c*) If an oxalate is treated with resorcinol[2] and H_2SO_4 (1 : 1) a blue color is obtained upon heating to fumes of SO_3. (*d*) If a solution of Mn^{++} is treated with a small amount of NaOH, then stirred to produce Mn^{+3}, the subsequent addition of $C_2O_4^{--}$ will produce a red color.[3]

9. Determination. — The oxalate ion may be precipitated as $CaC_2O_4 \cdot H_2O$, then (*a*) ignited to CaO which is weighed; (*b*) ignited below 600° to $CaCO_3$ which is weighed (p. 408, 9); (*c*) dissolved in dilute H_2SO_4 and titrated with $KMnO_4$.

$$5\ H_2C_2O_4 + 2\ KMnO_4 + 3\ H_2SO_4 = K_2SO_4 + 2\ MnSO_4 + 10\ CO_2 + 8\ H_2O$$

In certain cases oxalate may be decomposed to CO_2, which is determined as previously described (p. 450, 9). Oxalic acid may be determined volumetrically by titration with a standardized alkali, using methyl red or the potentiometric method for ascertaining the endpoint.

10. Oxidation and Reduction. — Oxalic acid is used chiefly as a reducing agent. Its properties as an oxidizing agent are of little importance. For a consideration of the various reactions see above (6).

§225. Hydrocyanic Acid. HCN

1. Physical Properties. — Hydrocyanic acid is a clear, mobile liquid, boiling at 26.5°; At −15° it freezes to a fibrous crystalline mass. Its density is 0.697 at 19°.[4] It burns with a blue-red flame, forming H_2O, CO_2 and N_2. The index of refraction is much lower than that of H_2O. The odor is characteristic, somewhat resembling that of bitter almonds. While HCN and the cyanides are very poisonous, their toxicity is popularly exaggerated.[5] The antidote is chlorine or ammonia by inhalation. An aqueous solution of HCN decomposes slowly, forming ammonium formate, $HCN + 2\ H_2O = HCOONH_4$. The reaction takes place less readily in the dark.[6] HCN is a weak acid, scarcely reddening litmus. Its salts are partially decomposed by CO_2. The free acid or a soluble salt, when warmed in a dilute alkaline or acid solution, becomes formic acid and ammonia, $HCN + 2\ H_2O = HCOOH + NH_3$. Hydrocyanic acid is used as an insecticide; its salts are used in the carburization of steel, in the manufacture of certain dyes, e.g., indigo, in the electrolytic deposition of certain metals, in the winning of Au,[7] etc.

[1] For additional details see: Curtman and Edmonds, *Ch. News*, **140**, 385–7 (1930), *C.A.* **24**, 4238.

[2] Chernoff, *J. Am. Ch. Soc.*, **42**, 1784 (1920).

[3] Sacher, *Ch. Ztg.*, **39**, 319 (1915), *C.A.* **9**, 2043. Cf. Caron and Raquet, *Ann. ch. anal. ch. appl.*, **24**, 205 (1919), *C.A.* **13**, 2494; Macri, *Boll. ch. farm.*, **59**, 73 (1920), *C.A.* **16**, 886 (1922).

[4] Bleekrode, *Proc. Roy. Soc.* (*London*), **37**, 339 (1884).

[5] In the analytical laboratory H_2S is a far greater potential danger than HCN because the toxicity of the latter has been over emphasized, while that of the former has been minimized or ignored.

[6] Cf. Nef, *Ann.*, **287**, 325 (1895).

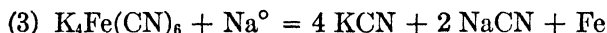
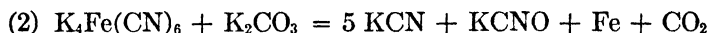
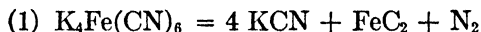
[7] Cf. Mellor, III, 499 (1923).

2. Occurrence. — The free acid does not occur in nature but in combination it is found in the kernels of many fruits, as bitter almonds, peaches, apricots, plums and cherries, also in the various parts of many plants. The roots of the mountain ash, when soaked in water for a time then distilled, yield HCN together with nitrobenzene.

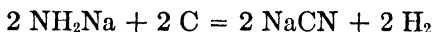
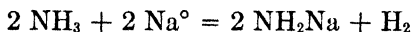
3. Preparation. — HCN may be prepared (*a*) by the action of dilute H_2SO_4 on an alkali cyanide;[1] by heating certain metal cyanides in a vacuum or at 100°; $2\ KCN + MgCl_2 + 2\ H_2O = 2\ KCl + Mg(OH)_2 + 2\ HCN$. Alkali cyanides may be prepared from $K_4Fe(CN)_6$ by (*a*) fusion in an iron crucible (Eq. 1), (*b*) heating with K_2CO_3 (Eq. 2), (*c*) reaction with Na° (Eq. 3).

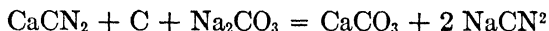
$$(1)\quad K_4Fe(CN)_6 = 4\ KCN + FeC_2 + N_2$$

$$(2)\quad K_4Fe(CN)_6 + K_2CO_3 = 5\ KCN + KCNO + Fe + CO_2$$

$$(3)\quad K_4Fe(CN)_6 + Na^\circ = 4\ KCN + 2\ NaCN + Fe$$

(*d*) In the sodamide process charcoal, NH_3 and Na° are heated at 300°–400° to form NH_2Na, then the temperature is raised to a red heat to obtain the cyanide:

$$2\ NH_3 + 2\ Na^\circ = 2\ NH_2Na + H_2$$

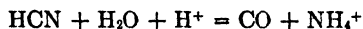
$$2\ NH_2Na + 2\ C = 2\ NaCN + 2\ H_2$$

(*e*) Starting with cyanamide, sodium cyanide is prepared by fusion with carbon and Na_2CO_3:

$$CaCN_2 + C + Na_2CO_3 = CaCO_3 + 2\ NaCN$$ [2]

5. Solubilities. — Hydrocyanic acid is miscible with water in all proportions. The cyanides of the alkali metals, alkaline earth metals, Hg^{++} and Au^{+3} are soluble in H_2O; $Ba(CN)_2$ is sparingly soluble. The solutions react alkaline, due to hydrolysis. Upon standing in the light a solution of KCN decomposes: $KCN + H_2O = HCOOK + NH_3$. Many of the heavy metal cyanides, insoluble in water, readily dissolve in an excess of CN^- with formation of a complex ion.

Certain metals (Pb, Hg, As, Sb, Sn, Bi and Cd) are dissolved by KCN with absorption of oxygen; others (Cu, Al, Fe, Co, Ni, Zn and Mg) are dissolved with evolution of hydrogen: $2\ Cu + 2\ KCN + 2\ H_2O = 2\ CuCN + 2\ KOH + H_2$; $CuCN + 3\ KCN = K_3Cu(CN)_4$.

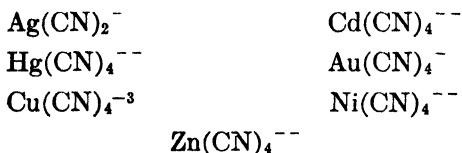
6. Reactions.[3] — There are two classes of complex cyanides formed by adding excess of CN^- to the precipitate initially obtained

[1] With concentrated H_2SO_4 decomposition takes place:

$$HCN + H_2O + H^+ = CO + NH_4^+$$

[2] For other methods see Beilstein, 4th ed., II, 33. Elöd and Nedelmann, *Z. Elektroch.*, **33**, 217–36 (1917), suggest a catalytic method.

[3] Cf. 6 *b* under the individual metals.

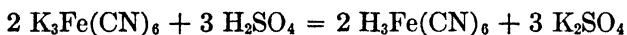
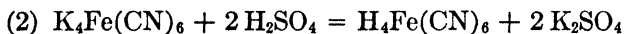
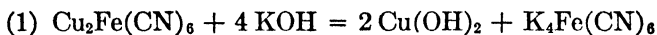
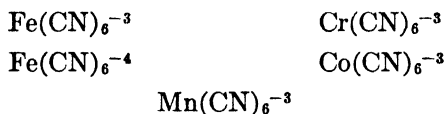
Class I. Complex cyanides that are not affected by alkali hydroxides but suffer decomposition when treated with dilute acids: $K_2Ni(CN)_4 + 2\ HCl = Ni(CN)_2 + 2\ KCl + 2\ HCN$. These closely resemble the complex iodides and thio-salts. The principal ions of this class are:

$Ag(CN)_2^-$	$Cd(CN)_4^{--}$
$Hg(CN)_4^{--}$	$Au(CN)_4^-$
$Cu(CN)_4^{-3}$	$Ni(CN)_4^{--}$
$Zn(CN)_4^{--}$	

Class II. Complex cyanides that, as precipitates, are transposed by alkali hydroxides in dilute solution (Eq. 1), and are converted to the acid without decomposition by dilute acids (Eq. 2). These more stable double cyanides correspond to the chloroplatinates (p. 237) and chloropalladates (p. 286). The most frequently occurring complex cyanides in this class are listed below.

$Fe(CN)_6^{-3}$	$Cr(CN)_6^{-3}$
$Fe(CN)_6^{-4}$	$Co(CN)_6^{-3}$
$Mn(CN)_6^{-3}$	

$$(1)\quad Cu_2Fe(CN)_6 + 4\,KOH = 2\,Cu(OH)_2 + K_4Fe(CN)_6$$

$$(2)\quad K_4Fe(CN)_6 + 2\,H_2SO_4 = H_4Fe(CN)_6 + 2\,K_2SO_4$$

$$2\ K_3Fe(CN)_6 + 3\ H_2SO_4 = 2\ H_3Fe(CN)_6 + 3\ K_2SO_4$$

The simple cyanides are transposed by the stronger mineral acids, more or less readily, with liberation of HCN, which escapes from a concentrated or hot solution. Mercuric cyanide reacts with H_2S to form HCN, but not with other acids. The cyanides of the alkali and alkaline earth metals are transposed by all acids — even CO_2 of the air — and give off HCN. Silver nitrate[1] precipitates CN^- (not from $Hg(CN)_2$) as silver cyanide, AgCN, white, insoluble in dilute HNO_3, soluble in NH_4OH, hot $(NH_4)_2CO_3$, excess CN^-, and $S_2O_3^{--}$ as in the case of AgCl. Cold, concentrated HCl decomposes AgCN with liberation of HCN (distinction from AgCl). When well washed, then gently ignited, AgCN does not melt, but forms metallic silver, soluble in HNO_3 (distinction and separation from AgCl). The complex $KAg(CN)_2$ is slowly decomposed by acetic acid, readily by HNO_3 and H_2SO_4, with precipitation of AgCN and liberation of HCN.

Solutions of mercurous ion react with CN^- to give Hg° and $Hg(CN)_2$ (distinction from Cl^-, Br^-, I^-). Ferrous ion, added to saturation, precipitates from solutions of cyanides (not from HCN) ferrous cyanide,

[1] Cf. Bassett and Corbet, *J. Ch. Soc.*, **125**, 1660 (1924).

$Fe(CN)_2$,[1] white if free from ferric iron, otherwise yellowish red due to $Fe(OH)_3$ (cf. p. 319). The precipitate is soluble in excess CN^- with formation of $Fe(CN)_6^{-4}$. Solutions of Fe^{+3} yield, with CN^-, a precipitate of ferric hydroxide and HCN. The latter may or may not be evolved. A small amount of the $Fe(OH)_3$ will dissolve in excess CN^-, forming $Fe(CN)_6^{-3}$.

The fixed alkali hydroxides, in boiling solution, strongly alkaline, gradually decompose the cyanides with production of NH_3 and a formate:

$$NaCN + 2\,H_2O = HCOONa + NH_3$$

Ferro- and ferricyanides finally yield the same products. Dilute alkali hydroxides transpose cyanides as in Class II, Eq. 1, above.

Cyanides are strong reducing agents. The action is especially vigorous in the fused state (cf. 7). Permanganates are reduced by cyanides, and $Cu(OH)_2$ in alkaline solution is changed to the lower valence. Solutions of cyanides, on exposure to the air, take up some O_2 to form a cyanate: $2\,NaCN + O_2 = 2\,NaCNO$. Commercial KCN usually contains potassium cyanate. Heating a cyanide with sulfur or $(NH_4)_2S_x$ results in the formation of a thiocyanate (cf. 8). HCN reduces PbO_2, forming $Pb(CN)_2$ and C_2N_2. Hydrogen peroxide reacts with HCN to form oxamide;[2] Cl_2 forms cyanogen chloride, CNCl: $HCN + Cl_2 = HCl + CNCl$; I_2 forms a similar product, but the reaction is not so marked. Concentrated H_2SO_4 decomposes all cyanides: $2\,HCN + H_2SO_4 + 2\,H_2O = 2\,CO + (NH_4)_2SO_4$.

7. Ignition. — On ignition, cyanides decompose in various ways. In some instances, as among the noble metals, the metal and cyanogen are formed; in others a carbide and nitrogen result; while in still others the metal, carbon and nitrogen are produced. Cyanides and all compounds containing cyanogen yield ammonia upon fusion with a fixed alkali. In a fused state cyanides are very efficient reagents for the liberation of metals from their oxides[3] or sulfides: $2\,KCN + SnO_2 = Sn^\circ + 2\,KCNO$. The cyanate or thiocyanate formed in the reaction is not readily decomposed by heat alone.

If an insoluble compound is to be tested for cyanide, a bead of $Na_2S_2O_3$ is first dehydrated on a platinum wire. It is then dipped in the unknown and heated until the sulfur begins to burn. Upon dipping the residue in a solution of ferric chloride, the blood-red color of ferric thiocyanate will appear if cyanide is present in the unknown.

8. Detection. — (*a*) The production of blue ferric ferrocyanide (Prussian blue) is considered a delicate test for cyanides. A small amount of the sample is treated with $FeSO_4$ and a few drops of an alkali. After shaking, a drop or two of $FeCl_3$ is added and the whole slightly acidified with H_2SO_4 (to dissolve the hydroxides) whereupon Prussian blue will appear if CN^-

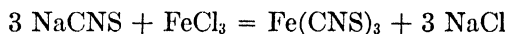
[1] Many investigators believe that this compound is not obtained except possibly momentarily, that the white precipitate is the polymer, ferrous ferrocyanide, $Fe_2Fe(CN)_6$ [or $(Fe(CN)_2)_3$]. Cf. Gmelin, 8th ed., No. 59, B, p. 560.

[2] Cf. Masson, *J. Ch. Soc.*, **91**, 1449–74 (1907).

[3] Cf. Hackspill and Grandadam, *Compt. rend.*, **180**, 930–2 (1925), *C.A.* **19**, 1805.

was in the original sample.[1] (*b*) The thiocyanate test is more delicate than that involving the formation of ferrocyanide. To the sample in an evaporating dish add 1–2 drops of yellow ammonium sulfide. Digest on the water-bath until the mixture is colorless and free from sulfide. Slightly acidify with HCl (which should not liberate any H_2S) and add a drop of $FeCl_3$. The blood-red color of ferric thiocyanate will appear if cyanide was present in the original material to the extent of one part in a million.[2]

$$NaCN + (NH_4)_2S_2 = NaCNS + 2\ NH_3 + H_2S$$

$$3\ NaCNS + FeCl_3 = Fe(CNS)_3 + 3\ NaCl$$

(*c*) Saturate a filter paper with a 4% alcoholic solution of guaiac. Allow the alcohol to evaporate. Moisten the paper with a 0.25% solution of $CuSO_4$ and let the unknown trickle over this test paper. A deep blue color indicates the presence of cyanide (Cl, Br, I and F interfere).[3] (*d*) To test for HCN in the air, moisten a piece of filter paper with benzidine acetate and cupric acetate. On exposure to air containing HCN for exactly 7 seconds the paper will turn blue if over 60 mg./cu.m. of HCN is present in the air. The reaction is not specific.[4] (*e*) Smith[5] has suggested that the formation of a reddish-brown color, when a cyanide is added to an alkaline picrate solution, will serve for the detection of one part of cyanide in 50 million.[6] (*f*) The detection of a cyanide in the presence of ferro- and ferricyanide is effected by slightly acidifying the sample, warming[7] and passing an inert gas (CO_2, H_2) through the solution. The HCN evolved may be collected in H_2O or an alkali and detected by methods already described.

9. Determination. — Cyanide is usually determined volumetrically by titration in an ammoniacal solution with standardized $AgNO_3$, using the formation of an opalescence of AgI as the endpoint. The reactions are:

[1] The test will detect one part of cyanide in 50,000 of solution. Cf. Kolthoff, *Z. anal. Ch.*, **57**, 1 (1918) who gives details for a modification of the original test.

[2] Under favorable conditions the test is even more delicate. Cf. Lavialle and Varenne, *J. pharm. ch.*, **17**, 97–102 (1918), *C.A.* **12**, 1159, who suggest calcium polysulfide in place of the ammonium salt.

[3] Cf. Kunz and Krause, *Z. anal. Ch.*, **55**, 467 (1916).

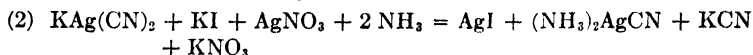
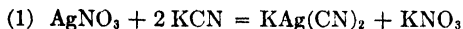
[4] Sieverts and Hermsdorf, *Z. angew. Ch.*, **34**, 3 (1921), *C.A.* **15**, 1269. Cf. Pertusi and Gastaldi, *Ch. Ztg.*, **37**, 609–10 (1913), *C.A.* **7**, 3292, who state that in the presence of Na_2HPO_4 the reaction is specific.

[5] Smith, R. G., *J. Am. Ch. Soc.*, **51**, 1171 (1929).

[6] Many critical examinations of the various tests for CN^- have been reported. Among them are the following: Gutzeit, *Helv. Ch. Acta*, **12**, 713–40 (1929), *C.A.* **23**, 4645; Sundberg, *Z. anal. Ch.*, **61**, 110–2 (1922), *C.A.* **16**, 1718; Ekeley and Macy [*C.A.* **14**, 161 (1920)]; Chelle, *J. pharm. Ch.*, **19**, 361 (1919), *C.A.* **13**, 2494; Kolthoff, *Pharm. Weekblad*, **54**, 1157–71 (1917), *C.A.* **12**, 30; Anderson, *Z. anal. Ch.*, **55**, 459 (1916).

[7] Ferro- and ferricyanides do not yield HCN under 80°.

(1) $AgNO_3 + 2\,KCN = KAg(CN)_2 + KNO_3$

(2) $KAg(CN)_2 + KI + AgNO_3 + 2\,NH_3 = AgI + (NH_3)_2AgCN + KCN + KNO_3$

10. Oxidation and Reduction. — Alkali cyanides in a fused state are powerful reducing agents (cf. 7). In solution alkaline oxidizing agents react with CN^- to give CNO^-; acid oxidizing agents usually form CO_2 and NH_4^+. For other reactions see above (6).

§226. Hydroferrocyanic Acid. $H_4Fe(CN)_6$

Anhydrous hydroferrocyanic acid is a white, crystalline, non-volatile solid, stable in dry air and readily soluble in water. The solution is sufficiently acidic to decompose carbonates.[1] It absorbs O_2 from the air, especially when warmed, evolving HCN and depositing Prussian blue: $7\,H_4Fe(CN)_6 + O_2 = Fe_4[Fe(CN)_6]_3 + 2\,H_2O + 24\,HCN$.[2]

Potassium ferrocyanide is the usual material employed in the preparation of $H_4Fe(CN)_6$ or any of the salts. It is obtained as a by-product in the coking of coal. Previously it was made by fusing nitrogenous animal matter (blood, hair, horn, hoof, etc.) with KOH and scrap iron then leaching the melt. The acid is formed upon addition of HCl to a solution of $K_4Fe(CN)_6$ and may be separated by ether extraction.[3]

The normal ferrocyanides of the alkalis and of the alkaline earths are readily soluble in water; those of the other metals are insoluble in water. There are many double (or mixed) ferrocyanides, some soluble and others insoluble: $Ca(NH_4)_2Fe(CN)_6$, 0.26 g./100 cc. H_2O; $Mg(NH_4)_2Fe(CN)_6$, 0.25 g./100 cc. H_2O; $MgK_2Fe(CN)_6$, 0.19 g./100 cc. H_2O, all at 17°. $SrK_2Fe(CN)_6$ and the corresponding barium salt are both only slightly soluble in water; the same is true of many other ferrocyanides having a heavy metal and an alkali for positive radicals. The soluble ferrocyanides are yellow in the hydrated state, white when anhydrous. The insoluble ferrocyanides vary in color as indicated in division 6 *b* under the various metals and in Table 40.

Insoluble ferrocyanides are transposed by alkalis (§225, 6, Class II). They are less easily oxidized than simple ferrous salts, yet are reducing agents of moderate strength, being themselves converted to ferricyanides. The $Fe(CN)_6^{-4}$ ion is not decomposed by cold, dilute acids to any great extent; in warm, acid solution, HCN is liberated. Soluble ferrocyanides and suspensions of insoluble ferrocyanides are decomposed when boiled with H_2O, HCN being evolved. The alkaline ferrocyanides are not decomposed in cold, aqueous solution by CO_2 (distinction from cyanides). A solution containing $Fe(CN)_6^{-4}$ may be treated with Na_2CO_3, then distilled in an atmosphere of CO_2 without evolution of HCN.

Ferrocyanides in acid solution are oxidized to ferricyanides by H_2O_2, PbO_2, $Cr_2O_7^{--}$, MnO_2, MnO_4^-, Co^{+3}, HNO_2, HNO_3,[4] Cl_2,[5] $HClO_3$, Br_2, $HBrO_3$, HIO_3[6] and many other reagents. Sulfuric acid[7] (3 : 1) heated with $Fe(CN)_6^{-4}$ forms HCN; a more concentrated acid decomposes all ferrocyanides with liberation of carbon monoxide.[8]

$$K_4Fe(CN)_6 + 6\,H_2SO_4 + 6\,H_2O = 6\,CO + 3\,(NH_4)_2SO_4 + 2\,K_2SO_4 + FeSO_4$$

[1] Cf. Kolthoff, *Ch. Weekblad*, **16**, 1409 (1919).

[2] Rudge, *Proc. Cambridge Phil. Soc.*, **16**, 467 (1912), states that at 100° partial decomposition takes place: $3\,H_4Fe(CN)_6 = 12\,HCN + Fe_2Fe(CN)_6$. Cf. Kolthoff, *loc. cit.*

[3] Cf. Gmelin, 8th ed., No. 59, B, p. 564–5 (1930), for other methods of preparation of $H_4Fe(CN)_6$.

[4] The product is $H_3FeNO(CN)_5$.

[5] Cf. del Fresno, *Z. Elektroch.*, **31**, 617 (1925).

[6] Cf. Schwicker, *Z. anal. Ch.*, **77**, 164 (1929).

[7] Cf. Gmelin, *loc. cit.*, p. 584 *et seq.*

[8] Cf. Chrétien, *Compt. rend.*, **141**, 37 (1905).

All ferrocyanides are decomposed on ignition; if anhydrous, N_2 and occasionally C_2N_2 escape; but if not completely dehydrated, HCN, CO_2 and NH_3 are liberated.

In analysis ferrocyanides are recognized by their reactions with Fe^{++}, Fe^{+3}, and Cu^{++} after precipitation of the $Fe(CN)_6^{-4}$ from dilute acid solution as $ThFe(CN)_6$;[1] from neutral solution as $KCeFe(CN)_6$;[2] from dilute HCl solution with $(NH_4)_2MoO_4$.[3] All of these methods have been recommended as separations from $Fe(CN)_6^{-3}$ and CNS^-.

Ferrocyanides may be determined in H_2SO_4 solution by titration with $KMnO_4$.[4] Gravimetric methods are unsatisfactory because practically all of the insoluble ferrocyanides are amorphous and difficult to filter.

TABLE 40

THE ACTION OF FERROCYANIDE ION ON VARIOUS CATIONS*

Cation	Product	Color, etc.
Pb^{++}	$Pb_2Fe(CN)_6$	white
Hg_2^{++}	$Hg_4Fe(CN)_6$	yellow → blue → gray, slowly decomp.
Hg^{++}	$Hg_2Fe(CN)_6$	white, quickly decomp.
Ag^+	$Ag_4Fe(CN)_6$	white, slowly turns blue
Bi^{+3}	$KBiFe(CN)_6$	white
Cu^{++}	$Cu_2Fe(CN)_6$	red brown
Cd^{++}	$Cd_3K_2[Fe(CN)_6]_2$	white
Sb^{+3}	K^+-Sb^{+3}-$Fe(CN)_6$	white
Sn^{++}	$Sn_2Fe(CN)_6$ (?)	white
Sn^{+4}	$SnFe(CN)_6$ (?)	white, gel.
Fe^{++}	$Fe_2Fe(CN)_6$ (?)	white if pure, usually pale blue
Fe^{+3}	$Fe_3[Fe(CN)_6]_2$ (?)	Prussian blue
Cr^{+3}	$Cr_4[Fe(CN)_6]_3$	gray green
Mn^{++}	$K_2MnFe(CN)_6$ (?)	pink
Zn^{++}	$Zn_3K_2[Fe(CN)_6]_2$	white, in neutral or sl. acid soln.
Co^{++}	$Co_2Fe(CN)_6$	green
Ni^{++}	$Ni_2Fe(CN)_6$	gray green
Ba^{++}	$BaK_2Fe(CN)_6$	white
Sr^{++}	$SrK_2Fe(CN)_6$	white
Ca^{++}	$Ca(NH_4)_2Fe(CN)_6$	white
Mg^{++}	$Mg(NH_4)_2Fe(CN)_6$	white

* Cf. Gmelin, 8th ed., No. 59, B, p. 593 *et seq.*

§227. Hydroferricyanic Acid. $H_3Fe(CN)_6$

Anhydrous hydroferricyanic acid is a non-volatile, crystalline solid, readily soluble in H_2O with formation of a brown solution which is strongly acid.[5] It is readily decomposed by heat. In the reaction of most ferricyanides with acids the $Fe(CN)_6^{-3}$ is destroyed;[6] alkalis are distinctly more effective in this respect.

[1] Browning and Palmer, *Am. J. Sci.*, [4] **23**, 448–50 (1907), *C.A.* **2**, 43.

[2] Banerjee, *J. Indian Ch. Soc.*, **6**, 259–62 (1929), *C.A.* **23**, 4907.

[3] Pavolini, *Ann. ch. applicata*, **19**, 561–2 (1929), *C.A.* **24**, 2691.

[4] Cf. Müller and Lauterbach, *Z. anal. Ch.*, **61**, 398 (1922).

[5] Müller, *Z. physik. Ch.*, **88**, 46 (1914); Kolthoff, *Ch. Weekblad*, **16**, 1406 (1919), have studied the strength of $H_3Fe(CN)_6$ as an acid.

[6] The decomposition of $Fe(CN)_6^{-3}$ is apparently not the simple reaction: $Fe(CN)_6^{-3} = Fe^{+3} + 6\ CN^-$, but one decidedly complex. Cf. Iimori, *Z. anorg. allgem. Ch.*, **167**, 168 (1927).

Potassium ferricyanide is usually employed in the preparation of most ferricyanides. It is obtained by oxidation of a ferrocyanide[1] (p. 461), evaporation and separation of the salt and repeated recrystallization from water. Large red crystals are finally secured that are readily soluble in H_2O and alcohol (distinction from $K_4Fe(CN)_6$). The free acid, $H_3Fe(CN)_6$, is made by adding concentrated HCl to a cold saturated solution of $K_3Fe(CN)_6$ and drying in a vacuum the precipitate that forms.[2] The product consists of lustrous, brownish-green needles, very soluble in H_2O and alcohol, more soluble in HCl than $H_4Fe(CN)_6$. An aqueous solution of $Fe(CN)_6^{-3}$ is fairly stable in the dark but decomposes in the light.[3]

The ferricyanides of the alkalis and alkaline earths are soluble in H_2O, those of most of the other metals are insoluble or slightly soluble. The soluble ferricyanides have a red color; those insoluble have different, pronounced colors. Potassium and sodium ferricyanides are not[4] precipitated from an aqueous solution by alcohol (separation from $Fe(CN)_6^{-4}$).

The reaction of $Fe(CN)_6^{-3}$ with various positive ions is given in Table 41.

TABLE 41

THE ACTION OF FERRICYANIDE ION ON VARIOUS CATIONS

Cation	Product	Color, etc.
Pb^{++}	*	no ppt. in neutral or acid soln.
Hg_2^{++}	? †	yellow, turning to gray
Hg^{++}	———	no ppt.
Ag^{+}	$Ag_3Fe(CN)_6$‡	brick red
Bi^{+3}	$BiFe(CN)_6$	brown
Cu^{++}	$Cu_3[Fe(CN)_6]_2$‡	greenish yellow, insol. in HCl
Cd^{++}	$Cd_3[Fe(CN)_6]_2$§	orange, distinction and sepn. from CNS^-
Sb^{+3}	Sb^{+5} and $Fe(CN)_6^{-4}$	———
Sn^{++}	?	white when pure, usually pale blue
Sn^{+4}	———	no ppt.
Fe^{++}	$Fe_3[Fe(CN)_6]_2$‖	Turnbull's blue
Fe^{+3}	———	brownish solution
Cr^{+3}	———	no ppt. In alk. soln. CrO_4^{--} and $Fe(CN)_6^{-4}$
Mn^{++}	$Mn_3[Fe(CN)_6]_2$‡	brown
Zn^{++}	$Zn_3[Fe(CN)_6]_2$	yellow
Co^{++}	$Co_3[Fe(CN)_6]_2$‡	red
Ni^{++}	$Ni_3[Fe(CN)_6]_2$‡	yellow
Ba^{++}	———	The various salts are readily soluble (distinction from $Fe(CN)_6^{-4}$)
Sr^{++}	———	
Ca^{++}	———	
Mg^{++}	———	

* Cf. Reihlen and Kummer, *Ann.*, **469**, 30 (1929).

† Composition of the precipitate apparently unknown. Cf. Luckmann, Dissert. Münster, 1908, p. 41.

‡ Kolthoff, *Z. anal. Ch.*, **62**, 214 (1923).

§ A more delicate test for Cd^{++} than S^{--}.

‖ Considered by many investigators to be identical with Prussian blue, both systems ultimately involving: $Fe^{++} + Fe(CN)_6^{-3} \rightleftarrows Fe^{+3} + Fe(CN)_6^{-4}$.

[1] Commercially the oxidation is effected with Cl_2 or PbO_2. Cf. Shcherbakov (*C.A.* **23**, 4147), for an electrolytic process.

[2] The acid may also be obtained by treating the lead salt with H_2SO_4 but not with H_2S. The latter would, of course, convert the Fe^{+3} to Fe^{++}. Cf. Müller, *J. prakt. Ch.*, [2] **84**, 364 (1911), for preparation from the silver salt.

[3] Cf. Gmelin, 8th ed., No. 59, B, p. 630.

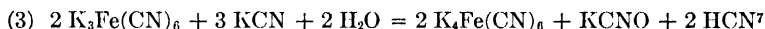
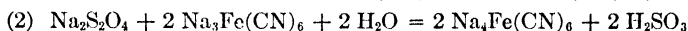
[4] Or to only a slight extent.

The action of $Fe(CN)_6^{-3}$ upon heating in alkaline solution is somewhat complex and depends largely on the specific conditions. Some of the possible products are $Fe(OH)_3$, NH_3, CO_2, $Fe(CN)_6^{-4}$, CN^-, CNO^-, etc.[1] Under similar conditions alkaline carbonates and bicarbonates give the same result as the hydroxides.

Nitric acid or an acid solution of NO_2^- reacts with $Fe(CN)_6^{-3}$ to give NO, CN^- and a nitroferricyanide (nitroprusside), $FeNO(CN)_5^{-2}$.[2,3] In alkaline solutions HPO_3^{--} and $H_2PO_2^-$ are oxidized to PO_4^{-3} while the $Fe(CN)_6^{-3}$ is reduced to $Fe(CN)_6^{-4}$. Sulfides (Eq. 1) reduce the iron of $Fe(CN)_6^{-3}$ to $Fe(CN)_6^{-4}$. Thiosulfates, when cold, have no effect on $Fe(CN)_6^{-3}$ but in a hot alkaline solution they reduce the iron to the lower valence. Sulfites, hydrosulfites (Eq. 2) and cyanides (Eq. 3) all produce a similar result. Sulfates[4] and persulfates[5] cause decomposition of $Fe(CN)_6^{-3}$.

(1) $6\ K_3Fe(CN)_6 + 3\ H_2S = 4\ K_4Fe(CN)_6 + K_2Fe^{II}Fe^{II}(CN)_6 + 6\ HCN + 3\ S$[6]

(2) $Na_2S_2O_4 + 2\ Na_3Fe(CN)_6 + 2\ H_2O = 2\ Na_4Fe(CN)_6 + 2\ H_2SO_3$

(3) $2\ K_3Fe(CN)_6 + 3\ KCN + 2\ H_2O = 2\ K_4Fe(CN)_6 + KCNO + 2\ HCN$[7]

Chlorides, under ordinary conditions, apparently do not affect $Fe(CN)_6^{-3}$, bromides tend to reduce the iron, while iodides[8] form an (unstable) addition compound which decomposes to give ferrocyanide ion and free iodine. Hypochlorites, chlorates and hypobromites decompose ferricyanides usually with the formation of some nitroferricyanide, the amount decreasing with an increase in temperature.

Potassium ferricyanide is reduced to the ferrocyanide by the metals[9] Pd, Th, Mg and As, but not by Pb, Hg, Ag, Sb, Au, Pt, Bi, Cu, Cd, Te, Al, Fe, Co, Mn and Zn. When a piece of any metal except Au and Pt is placed in contact with a solution of $Fe(CN)_6^{-3}$ and Fe^{+3} a coating of Prussian blue is soon formed. Pb^{++}, Sn^{++}, Cr^{+3} and Mn^{++} in alkaline solution all reduce $Fe(CN)_6^{-3}$ to $Fe(CN)_6^{-4}$.

All ferricyanides undergo decomposition similar to that of the corresponding ferrocyanides when ignited.

Ferricyanides in solution are detected by their reaction with Fe^{++} and Fe^{+3}. Ferricyanides may be separated (*a*) from ferrocyanides by precipitating the latter as $ThFe(CN)_6$, or as a double salt of Tl^+ and Ca^{++}; (*b*) from thiocyanates by precipitation of the $Fe(CN)_6^{-3}$ as $Cd_3[Fe(CN)_6]_2$.[10]

Ferricyanides may be determined by reduction to the ferrocyanide with KI in acid solution and titration of the I_2 with standardized thiosulfate.

§228. Cyanic Acid. HCNO

Cyanic acid is a colorless liquid, giving off a pungent, irritating vapor; it is stable only at low temperatures. The density of the liquid is 1.140 at 0°. Gaseous cyanic acid dissolves in ice water, the stability of the solute varying inversely with the concentration. In aqueous solutions cyanic acid has the structure H · O · C ⋮ N; in the vapor state and dissolved in ether the formula is O : C : N · H.[11]

Cyanates of the alkalis and of the Group IV metals may be made by passing cyanogen

[1] Cf. Grube, *Z. anorg. allgem. Ch.*, **84**, 190 (1913).

[2] This latter has been recommended for the detection of S^{--}.

[3] Cf. Benedetti-Pichler, *Z. anal. Ch.*, **70**, 271 (1927).

[4] Kelley and Bohn, *J. Am. Ch. Soc.*, **41**, 1776 (1919).

[5] Belluci and Ricca (*C.A.* **18**, 2849).

[6] Venditori, *Atti accad. Lincei*, [5] **15**, I, 370 (1906).

[7] The oxidation is effected in alkaline solution; Treadwell, *Z. anorg. allgem. Ch.*, **71**, 219 (1911).

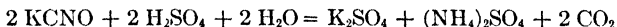
[8] Cf. Rosenheim and Dehn, *Ber.*, **48**, 1178 (1915).

[9] Cf. Smith, *Z. anorg. allgem. Ch.*, **82**, 63–70 (1913).

[10] Browning and Palmer, *Am. J. Sci.*, [4] **23**, 448 (1907), *C.A.* **2**, 43.

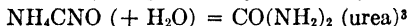
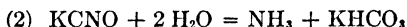
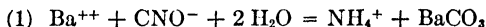
[11] Regarding the constitution of cyanates see Nef, *Ann.*, **287**, 355 (1895); also Beilstein, 4th ed., III, 31.

gas into the hydroxides. Cyanates are also readily obtained by the action of mild oxidizing agents on cyanides in the dry state: $KCN + PbO = KCNO + Pb$.[1] The salt may be extracted with ether. Cyanic acid cannot be prepared by transposing metallic cyanates with the stronger acids in the presence of H_2O: $HCNO + H_2O = NH_3 + CO_2$. Cyanates, therefore, when treated with HCl or H_2SO_4, effervesce with the escape of CO_2 (distinction from cyanides), the pungent odor of cyanic acid being perceptible:

$$2\,KCNO + 2\,H_2SO_4 + 2\,H_2O = K_2SO_4 + (NH_4)_2SO_4 + 2\,CO_2$$

Cyanates may be divided into two major classes, depending upon their reaction with H_2O: (*a*) those forming insoluble carbonates (Eq. 1), and (*b*) those forming soluble carbonates (Eq. 2).[2]

(1) $Ba^{++} + CNO^- + 2\,H_2O = NH_4^+ + BaCO_3$

(2) $KCNO + 2\,H_2O = NH_3 + KHCO_3$

$NH_4CNO\ (+ H_2O) = CO(NH_2)_2$ (urea)[3]

The cyanates of the alkali metals are soluble in water; most of the others are insoluble to slightly soluble. When freshly prepared, solutions of the alkali cyanates react neutral to phenolphthalein.[4] They gradually decompose on standing, with evolution of NH_3 (and CO_2). Potassium cyanate treated with bromine in aqueous solution gives KBr, NH_4Br, N_2 and CO_2;[5] with NaBrO a carbonate, formate, and N_2 are obtained. Calcium cyanate heated to 80° in aqueous solution forms $CaCO_3$ and urea, $CO(NH_2)_2$.[6]

Lead cyanate may be prepared by treating potassium cyanate with $Ba(NO_3)_2$ to remove any CO_3^{--} present, then adding $Pb(NO_3)_2$ to the filtrate. The lead cyanate precipitated is comparatively stable and serves well for the preparation of cyanic acid. Silver cyanate is a white solid, soluble in water to the extent of 0.0075 g./100 cc. at 22°, readily soluble in NH_4OH. Treated with iodine in aqueous solution and warmed, silver cyanate reacts to form AgI, $AgIO_3$, CO_2 and urea.

Apparently all cyanates of the heavy metals when heated give CO_2 and the metal derivative of cyanamide. Alkali cyanates (not ammonium cyanate) may be heated almost to a dull red without decomposition. At 900° the potassium salt is 50% converted to KCN in two hours.[7]

The detection of cyanic acid has been studied by Ripan,[8] the determination may be effected by addition of excess $AgNO_3$ and titration of the excess,[9] or by decomposition with H_2SO_4 and titration of the excess acid with NaOH.[10]

§229. Thiocyanic Acid. HCNS or HSCN

At room temperature thiocyanic acid, HCNS,[11] is a gas that is stable for about a day. If cooled, the gas condenses to a white pungent smelling mass of crystals stable for only a short time. The solid melts at + 5° forming a liquid that readily polymerizes to a yel-

[1] Liebig, *Ann.*, **41**, 289 (1842); cf. Beilstein, 4th ed., III, 32.

[2] Masson and Masson, *Z. physik. Ch.*, **70**, 290–314 (1910), *C.A.* **4**, 1581.

[3] In 0.1 *N* aqueous solution ammonium cyanate is 92% converted to $CO(NH_2)_2$; Walker and Hambly, *J. Ch. Soc.*, **67**, 746 (1895). For the rate of conversion see: Walker, *Proc. Roy Soc.* (*London*), **87**, 543 (1912).

[4] Mauguin and Simon, *Compt. rend.*, **169**, 385 (1919).

[5] Normand and Cummings, *J. Ch. Soc.*, **101**, 1863 (1912).

[6] Masson and Masson, *loc. cit.*, p. 302.

[7] Portevin, *Compt. rend.*, **161**, 309 (1915).

[8] Ripan, *Bul. soc. stiinte Cluj*, **4**, 144–53 (1928), *C.A.* **23**, 2905. Cf. Fossé, *Compt. rend.*, **171**, 635–7 (1920), *C.A.* **15**, 217.

[9] Walker and Hambly, *J. Ch. Soc.*, **67**, 747 (1895).

[10] Mauguin and Simon, *Compt. rend.*, **169**, 385 (1919), *C.A.* **13**, 2824.

[11] There is no structural implication. This formula is given because it is the one usually found in inorganic literature.

low solid. Thiocyanic acid is soluble in water, but the solution is unstable unless dilute. A concentrated solution decomposes to give HCN and yellow crystals of perthiocyanic acid, $C_2N_2S_3H_2$. When HCNS is boiled with a dilute acid some distils over, the balance is decomposed. In cold, aqueous solution, however, HCNS is fairly stable toward mineral acids if not too concentrated. HCNS is a strong, monobasic acid, nearly as highly dissociated as the halogen acids.

Several methods have been suggested for the preparation of HCNS. An aqueous solution may be obtained by (*a*) treating $Pb(CNS)_2$ with H_2S and removing the PbS by filtration, (*b*) removing the barium from solution of $Ba(CNS)_2$ by addition of the calculated amount of H_2SO_4.[1] Thiocyanates may be prepared by fusion of the cyanide with free sulfur, KCN + S = KCNS. Ammonium thiocyanate is readily made from NH_3 and CS_2: $4\ NH_3 + CS_2 = NH_4CNS + (NH_4)_2S$. Technically NH_4CNS is a by-product of the manufacture of fuel gas.

The thiocyanates of the alkalis, the alkaline earths and most of the metals are soluble in water. Silver, lead, thallous and cuprous thiocyanates are insoluble; mercuric and stannous[2] thiocyanates are only slightly soluble in H_2O. (The solubility in 100 cc. of H_2O at about 20° is: AgCNS, 0.0_425 g.; $Pb(CNS)_2$, 0.045 g.; TlCNS, 0.0315 g.; $Cu_2(CNS)_2$, 0.0_35 g.; $Hg(CNS)_2$, 0.07 g.) All of these thiocyanates are soluble in excess of the reagent with formation of double salts, e.g., $K_2Ag(CNS)_3$, $K_3Ag(CNS)_4$, $K_2Hg(CNS)_4$, etc.

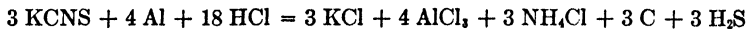
The reaction of CNS^- with ions of the various metals is given in Part II under subsection 6 b of each metal (see especially, Hg, Ag, Pb, Cu, Pt, Fe and Co). In microscopic analysis the double salt $K_2Hg(CNS)_4$ is used as a "group reagent," particularly for the detection of Cu^{++}, Cd^{++}, Fe^{+3}, Co^{++} and Zn^{++}.

Certain active oxidizing agents, viz., nascent chlorine, and HNO_3 containing nitrogen oxides, acting in hot, concentrated solutions of thiocyanates, precipitate perthiocyanogen, $C_3N_3S_3H$, of a yellow to red color, sometimes even blue. It may be formed in the test for iodine, and mistaken for that element, in starch or CS_2. If boiled with a solution of KOH it forms thiocyanate.

Concentrated HCl or H_2SO_4, added in excess to an aqueous solution of CNS^-, causes the gradual formation of a yellow precipitate of perthiocyanic acid, $C_2N_2S_3H_2$, slightly soluble in hot H_2O from which it crystallizes in yellow needles. It dissolves in alcohol and in ether.

Potassium thiocyanate can be fused in a vacuum with only slight decomposition, but exposed to the air it is resolved into a sulfate and cyanate with evolution of SO_2. With other cations N_2, C_2N_2, CS_2, or a metal sulfide may be formed.

When thiocyanic acid is oxidized the final product, so far as the sulfur is concerned, is always H_2SO_4 or a sulfate. In many cases it has been shown that the cyanogen is evolved as HCN. Under suitable conditions the reaction is quantitative with HNO_3, Br_2, NaBrO and I_2 + $NaHCO_3$. **PbO_2** and **Pb_3O_4** form Pb^{++} and H_2SO_4 in acid solution only. An alkaline thiocyanate with **PbO** forms CNO^-; **H_3AsO_4**, $Cr_2O_7^{--}$, **Co^{+3}** and **Ni^{+4}** are reduced to the lower valence with formation of H_2SO_4. Higher valences of **Mn** in acid solution form Mn^{++}, HCN and H_2SO_4. In alkaline mixture a cyanate and sulfate are formed. **Nitrous** or **nitric** acid forms H_2SO_4 and nitric oxide. **Chlorine, $KClO_3$ + HCl**, $S_2O_8^{--}$, or **H_2O_2** in acid or neutral solution forms H_2SO_4 and HCN except that under some conditions, NH_3, S or perthiocyanogen may also be formed. **$HBrO_3$** forms HBr and H_2SO_4. **HIO_3** forms H_2SO_4 and free iodine which may react further to form cyanogen iodide. Treated with Zn° and an acid, thiocyanates yield H_2S; carbon disulfide, ammonia, methyl amine and a number of other products may also be obtained. The distillation of a thiocyanate with Al° and HCl quantitatively decomposes the CNS^- into NH_3, C and H_2S:

$$3\ KCNS + 4\ Al + 18\ HCl = 3\ KCl + 4\ AlCl_3 + 3\ NH_4Cl + 3\ C + 3\ H_2S$$

The detection of CNS^- may be effected by means of the red color produced with Fe^{+3} [3]

[1] Cf. Beilstein, 4th ed., III, p. 142. For the preparation of pure HCNS see: Rück and Steinmetz, *Z. anorg. allgem. Ch.*, **77**, 51–89 (1912), *C.A.* **6**, 3378.

[2] Söderbäck, *Ann.*, **419**, 290 (1919).

[3] For delicacy (about 0.1 mg. CNS^-) see Curtman and Harris, *J. Am. Ch. Soc.*, **38**, 2622–9 (1916).

or the blue with a trace of Co^{++}.[1] If to a solution of CNS^- a few drops of 20% alcoholic α-naphthol are added, then some concentrated H_2SO_4, at first a green color is produced. On shaking, it changes to violet.[2] Tincture of guaiac becomes blue when added to a solution of Cu^{++} and CNS^-. Thiocyanate ion may be separated from ferro- and ferricyanide ions by precipitating them with Zn^{++}.[3] Perciabosco states that ferrocyanide may also be removed by addition of an excess of Fe^{+3}. Upon filtration the red color of the ferric thiocyanate is observed in the filtrate[4] (or without filtration shaking with amyl alcohol will extract the red compound).

Thiocyanates may be determined (*a*) *gravimetrically* by precipitation as AgCNS, drying and weighing as such, or by oxidation of the CNS^- to SO_4^{--}, precipitation as $BaSO_4$, drying and weighing as such. (*b*) *Volumetrically,* Volhard's[5] procedure is a classical one. This involves titration of the CNS^- with $AgNO_3$, an excess being added. The excess is determined by back titration with standardized CNS^- using Fe^{+3} as an indicator. The titration of CNS^- with $CuSO_4$ in the presence of $NaHSO_3$ has been recommended.[6] The bromate method, involving addition of $KBrO_3$ and KBr followed by titration of the Br, has also been advocated.[7] (*c*) *Colorimetrically,* CNS^- may be determined by comparing the red color of ferric thiocyanate with a standard.

§230. Nitrogen (Gr. *nitron* = nitre). N = 14.008. Atomic No. 7. Recognized as a simple gas by Lavoisier about 1776.

1. Physical Properties. — Density of the liquid at −195.5°, 0.8042; of the solid at −252.5°, 1.0265; melting point, −210°; boiling point, −195.7°. Liquid nitrogen is colorless and transparent. The gas is tasteless, odorless, colorless, and is not poisonous. It does not burn or support combustion. It is very inert, not attacking other free elements under ordinary conditions.

2. Occurrence. — Nitrogen constitutes, by volume, about four-fifths of the atmosphere. It is found in the lithosphere to only a slight extent, as a nitrate, e.g., Chile saltpeter, and in various forms as a constituent of animal and vegetable matter.

3. Preparation. — (*a*) Liquefaction of the air by the Linde process, followed by boiling the liquid to separate the various components, is capable of yielding nitrogen 99.5% pure. (*b*) The Casale process involves burning hydrogen in air to remove the oxygen. The N_2 after further purification, may be used for the synthesis of NH_3. (*c*) Ammonium nitrate heated in glycerine gives an almost quantitative yield of N_2. (*d*) Fairly pure N_2 may be prepared by means of the reaction $8\,NH_3 + 3\,Cl_2 = 6\,NH_4Cl + N_2$. The ammonia must always be kept in excess, otherwise the very explosive NCl_3 will form. (*e*) A warm solution of calcium hypochlorite treated with NH_3 yields N_2: $3\,Ca(ClO)_2 + 4\,NH_3 = CaCl_2 + 2\,N_2 + 6\,H_2O$. (*f*) Ignition of ammonium dichromate forms N_2: $(NH_4)_2Cr_2O_7 = N_2 + Cr_2O_3 + 4\,H_2O$.[8]

4. Hydrides,[9] Oxides and Hydroxides. — *Hydrazoic acid* (azoimide, hydronitric acid), N_3H, is a colorless, mobile liquid of a penetrating odor. It has a very irritating effect upon the skin. It readily explodes with marked violence, boils at 37°, and in the solid state melts at −80°. It is soluble in water and alcohol. The aqueous solution is

[1] For delicacy see Górski, *Z. anorg. allgem. Ch.*, **81**, 328 (1913).
[2] Colasanti, *Gazz. ch. ital.*, **20**, 303 (1890).
[3] Feigl, *Ch. Ztg.*, **38**, 1265 (1914). Cf. Browning and Palmer, *Am. J. Sci.*, [4] **23**, 448 (1907).
[4] Perciabosco, *Ann. ch. applicata*, **13**, 346 (1923), *C.A.* **18**, 2300.
[5] Volhard, *Ann.*, **190**, 1 (1878).
[6] Rosanoff and Hill, *J. Am. Ch. Soc.*, **29**, 1474 (1907).
[7] Treadwell and Mayr, *Z. anorg. allgem. Ch.*, **92**, 127 (1915).
[8] The reaction is probably not as simple as indicated.
[9] Ammonia has been discussed in §207, p. 423, *et seq.*

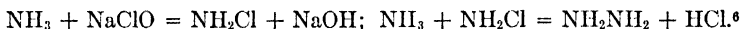
fairly stable, but when boiled with a mineral acid it slowly decomposes to form N_2 and an ammonium salt. The constitution of hydrazoic acid is probably N⋮N : N · H.[1]

The preparation of hydrazoic acid may be effected by (*a*) passing dry NH_3 over Na° at 250°–350°, then treating the resulting sodamide, $NaNH_2$, with nitrous oxide ($2\ NH_3 + 2\ Na^\circ = 2\ NaNH_2 + H_2$; $NaNH_2 + N_2O = NaN_3 + H_2O$);[2] (*b*) treating hydrazine with H_2O_2;[3] (*c*) the action of nitrous acid on hydrazine hydrochloride ($N_2H_4 \cdot HCl + HNO_2 = N_3H + 2H_2O + HCl$).

Azoimide is an acid of marked activity, dissolving a number of metals with evolution of hydrogen. The azides of the alkali metals (NaN_3, KN_3, etc.) are readily soluble in H_2O; those of the alkaline earths (MgN_6, CaN_6, etc.) are also soluble, while those of the other metals are slightly soluble to insoluble. The alkali and alkaline earth salts are not explosive; the others are. Silver azide, AgN_3, white, is somewhat similar in properties to the silver halides, especially AgCl and AgBr. Cu^{++} forms a red-brown precipitate of CuN_6. With Fe^{+3} a red solution of FeN_9 is obtained. Potassium permanganate reacts with N_3H to form N_2 and H_2O. The acid is readily reduced by $Zn^\circ + H^+$ or by $Fe(OH)_2$ to NH_3 and N_2H_4; H_2S forms N_2 and NH_3. Potassium azide may be used to separate quantitatively Th^{+4} from Ce, La, Nd and Pr.[4]

Hydrazoic acid may be determined by treatment with HNO_2 or I_2 and measurement of the N_2 evolved.[5]

Hydrazine, N_2H_4, is a colorless, hygroscopic liquid, boiling at 113.5° and solidifying at slightly above 0°. Its density is slightly greater than that of water. Like sulfuric acid hydrazine vigorously reacts with H_2O to form the monohydrate which may be diluted further as desired. As a solvent N_2H_4 is similar to ammonia. It is decomposed by heating into N_2 and NH_3. Hydrazine is probably best prepared by the interaction of ammonia and sodium hypochlorite in the presence of a small amount of glue as a protective colloid. The N_2H_4 may be removed from the solution by addition of H_2SO_4 which forms the slightly soluble hydrazine sulfate, $N_2H_4 \cdot H_2SO_4$. The principal reactions are:

$$NH_3 + NaClO = NH_2Cl + NaOH; \quad NH_3 + NH_2Cl = NH_2NH_2 + HCl.$$ [6]

Hydrazine is a strong reducing agent, precipitating Hg°, Ag° and Au° from solution; Cu^{++} in an acid medium is changed to Cu_2^{++}, in alkaline solution, i.e., Fehling's solution, it becomes Cu° (separation from Sn and Zn); Fe^{+3} forms Fe^{++}, I_2 gives HI, etc. Solutions of ClO_3^-, BrO_3^- or IO_3^- may be boiled with N_2H_4 without reaction;[7] the presence of a little CuO, however, produces immediate reduction even in the cold: $2\ KClO_3 + 3\ N_2H_4 \cdot HNO_3 = 3\ N_2 + 3\ HNO_3 + 2\ KCl + 6\ H_2O$.[8] In general the oxidation of N_2H_4 will take place in one of three ways depending on the reagent used and also upon the conditions. (1) With H_2O_2, $KClO_3$ or $K_2S_2O_8$ the products are hydrazoic acid and a small amount of ammonia. (2) $KMnO_4$, MnO_2 or Fe_2O_3 produces ammonia and a little hydrazoic acid. (3) KIO_3, HgO or $HgCl_2$ gives only a small amount of both ammonia and hydrazoic acid.[9] Hydrazine may be determined by titration with $KMnO_4$.

The oxides of nitrogen are: *nitrous oxide*, N_2O; *nitric oxide*, NO; (nitrogen sesquioxide, N_2O_3); *nitrogen di-* or *tetroxide*, NO_2 or N_2O_4; (nitrogen pentoxide, N_2O_5). In number and valence type they closely resemble the oxygen compounds of vanadium. The first two oxides, N_2O and NO, are neutral; the higher oxides are acid anhydrides forming, upon hydration, HNO_2 and HNO_3. All of the oxides may be ob-

[1] Cranston and Livingstone, *J. Ch. Soc.*, **1926**, 501; Turrentine, *J. Am. Ch. Soc.*, **36**, 23–35 (1914).

[2] Wislisenus, *Ber.*, **25**, 2084 (1892).

[3] Browne, *J. Am. Ch. Soc.*, **27**, 551 (1905).

[4] Dennis, *J. Am. Ch. Soc.*, **18**, 947 (1896).

[5] Cf. Raschig, *Ch. Ztg.*, **32**, 1203 (1908).

[6] Joyner, *J. Ch. Soc.*, **123**, 1114 (1923); Raschig, *Ch. Ztg.*, **31**, 926 (1907).

[7] Iodates react with N_2H_4 in strongly acid solution.

[8] Hodgkinson, *J. Soc. Ch. Ind.*, **13**, 815 (1914).

[9] Browne and Shetterly, *J. Am. Ch. Soc.*, **31**, 222, 783 (1909). Cf. Browne and Welch, *Ibid.*, **33**, 1728 (1911); Friedrichs, *Ibid.*, **35**, 244 (1913); Schlenk and Weichselfelder, *Ber.*, **48**, 669 (1915).

tained, under suitable conditions, by the action of metals or other reducing agents on HNO_3.[1]

Nitrous oxide, N_2O, is a colorless gas with a slightly sweet smell and taste. Its critical temperature is 36.5°, critical pressure, 71.66 atmospheres.[2] It can be liquefied at 0° under a pressure of three atmospheres. When breathed in small amounts N_2O produces a mild exhilaration, hence the name "laughing gas"; in larger quantities (mixed with 25% oxygen) N_2O acts as a shallow anaesthetic and is used in dentistry for that purpose. As a rule, anything that burns in air will also burn in nitrous oxide, since decomposition ($2\ N_2O = 2\ N_2 + O_2$), starting at about 500° and complete at about 900°, gives a mixture richer in oxygen: $2\ N_2 : O_2$, whereas air is $4\ N_2 : O_2$. Nitrous oxide is prepared by (1) heating NH_4NO_3 at about 200° ($NH_4NO_3 = N_2O + 2\ H_2O$); (2) heating a mixture of $(NH_4)_2SO_4$ and $NaNO_3$ at 240°; (3) boiling a mixture of five parts $SnCl_2$, ten parts HCl (sp. g. 1.21) and nine parts HNO_3 (sp. g. 1.3). ($2\ HNO_3 + 4\ SnCl_2 + 8\ HCl = 4\ SnCl_4 + N_2O + 5\ H_2O$.[3]) At lower temperatures ($< 350°$) N_2O is a vigorous oxidizing agent. Although nitrous oxide may be obtained from hyponitrous acid by dehydration ($H_2N_2O_2 \rightarrow N_2O + H_2O$) it does not combine with H_2O or hydroxides to form this acid or its salts. Nitrous oxide may be distinguished from oxygen by its faint odor, taste and inertness toward NO. The determination of N_2O may be effected by passing the gas over red-hot iron and measuring the N_2 formed.

Nitric oxide, NO, is a colorless gas, heavier than air and somewhat soluble in H_2O. The solution formed is neutral. The gas can be cooled to a colorless liquid boiling at −153.6°. The critical temperature is −92.9°, critical pressure 64.4 atmospheres. The odor and taste of NO are unknown because of its immediate conversion to NO_2 (see below) on exposure to the air. Nitric oxide is more stable than nitrous oxide, being decomposed but slightly when heated to 900°. Nitric oxide is moderately soluble in water, readily soluble in a 16% solution of $FeSO_4$, forming the "brown ring," which is decomposed at 100°. Among the best methods for the preparation[4] of NO are (1) treating Hg° with a mixture of HNO_3 and H_2SO_4;[5] (2) adding H_2SO_4 (1 : 1) dropwise to a concentrated solution of two parts KNO_2, and one part KI ($2\ HNO_2 + 2\ HI = 2\ NO + I_2 + 2\ H_2O$);[6] (3) dropping HNO_3 (sp. g. 1.2) on a mixture of Cu° and Pt°.[7] When exposed to the air NO ultimately becomes NO_2, the action not being direct, as indicated by the equation: $2\ NO + O_2 = 2\ NO_2$, but probably stepwise and involving the formation of the intermediate compound N_2O_3.[8] Nitric oxide, as indicated above, does not combine directly with H_2O to form an acid. It cannot, however, be kept over water because of the action of dissolved oxygen and the H^+,[9] which on long contact produce HNO_2, along with $H_2N_2O_2$ and ultimately N_2.

When heated in NO at 450°, Ag°, Hg° and Al° are not affected; filings of Cu°, Fe°, Cd° and Zn° are superficially oxidized, but Pb° is completely changed to PbO. If the metals are in a very fine state of division, Ni°, Fe° and Cu° will form the lower oxide, NiO, FeO and Cu_2O respectively. Upon long contact with KOH nitric oxide will form KNO_2 and N_2O; above 125° the reaction is more rapid but the products are KNO_2 and N_2.[10] Nitric oxide can be reduced stepwise to NH_3 and can be oxidized to higher valences, the reactions being, however, rather complex.[11] Stannous tin in acid solution changes NO to

[1] Concerning nitrogen oxides see: Daniels, *et al.*, *J. Am. Ch. Soc.*, **44**, 2402 (1922); Lueck, *Ibid.*, p. 757; Foerster, *Ber.*, **55B**, 490 (1922); Briner, *et al.*, *Helv. Ch. Acta*, **5**, 432 (1922).

[2] Cardoso and Arni, *J. ch. phys.*, **10**, 504 (1912).

[3] Campari, *J. Ch. Soc.*, **56**, 569 (1889).

[4] Moser, *Z. anal. Ch.*, **50**, 401–33 (1911), *C.A.* **5**, 3387.

[5] Emich, *Monatsh.*, **13**, 73 (1892).

[6] Winkler, *Ber.*, **34**, 1408 (1901).

[7] Baxter and Hickey, *Am. Ch. J.*, **33**, 300 (1905).

[8] Cf. Friend, VI, 1, p. 156.

[9] Moser, *loc. cit.* See, however, Nichols and Morse, *J. Phys. Ch.*, **35**, 1239–52 (1931); Sanfourche, *Compt. rend.*, **168**, 401–4 (1919), *C.A.* **13**, 1055.

[10] For an explanation of the behavior of NO toward the caustic alkalis, see Foerster, *Ber.*, **55B**, 490–1 (1922), *C.A.* **16**, 1712.

[11] Briner and Fridöri, *J. ch. phys.*, **16**, 279 (1918), *C.A.* **13**, 100.

NH_2OH and NH_3; in alkaline solution the product is $H_2N_2O_2$. Hydriodic acid reduces NO to NH_3; H_2SO_3 and H_2S[1] form N_2O; Ag_2O, MnO_2, PbO_2, $KMnO_4$, I_2 and HClO oxidize NO to HNO_3; hydrogen peroxide yields HNO_2 and HNO_3. Nitric oxide is absorbed by solutions containing Fe^{++}, Ni^{++}, Co^{++}, or Mn^{++}. In the case of Fe^{++} a brown color is obtained, but there is no change with the other ions.[2]

Nitric oxide is easily detected by the formation of brown fumes when it comes in contact with the air. It may be determined (1) by measurement of the volume contraction due to reaction with O_2 in the presence of solid KOH, or (2) by titration with standardized $KMnO_4$. Either method fails for mixtures of nitrogen oxides.

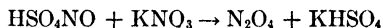
Nitrogen sesquioxide,[3] N_2O_3, at room temperature is a brown gas, behaving as though it were a mixture of NO_2 and NO. At low temperatures it is an indigo blue liquid. It is apparently insoluble in water but decomposes into NO and NO_2 which do dissolve.[4] It is formed upon treating NO with a small amount of oxygen: $4\ NO + O_2 = 2\ N_2O_3$. More oxygen produces N_2O_4: $2\ N_2O_3 + O_2 = 2\ N_2O_4$. Dry NaOH absorbs N_2O_3 completely: $N_2O_3 + 2\ NaOH = 2\ NaNO_2 + H_2O$. H_2S reacts with N_2O_3 to give S° and SO_2.

Nitrogen di- or *tetroxide,* NO_2 or N_2O_4,[5] below −10° is a white crystalline solid; between −10° and 21.3° a liquid varying from colorless to a dark orange as the temperature rises. Above 21.6° it is a poisonous gas that does not support combustion. At the boiling point N_2O_4 is about one-fifth dissociated into NO_2, at 135° the dissociation is almost complete and at a slightly higher temperature decomposition into $NO + O_2$ begins:

$$N_2O_4 \text{ (colorless)} \rightleftarrows 2\ NO_2 \text{ (brown)} \rightleftarrows 2\ NO + O_2 \text{ (colorless)}$$[6]

The preparation of N_2O_4 is effected by the thermal decomposition of $Pb(NO_3)_2$ or by the interaction of nitrosylsulfuric acid and dry KNO_3:[7]

$$2\ Pb(NO_3)_2 \rightarrow 2\ PbO + 2\ N_2O_4 + O_2$$

$$HSO_4NO + KNO_3 \rightarrow N_2O_4 + KHSO_4$$

Nitrogen tetroxide dissolves in water forming a green-blue solution containing HNO_3 and HNO_2. The latter reacts further to give N_2O_3 or $HNO_3 + NO$, depending upon the dilution. Reaction of NO_2 with a fixed alkali produces a nitrate and a nitrite: $2\ NO_2 + 2\ NaOH = NaNO_2 + NaNO_3 + H_2O$; with CaO the reaction is: $2\ CaO + 5\ NO_2 = 2\ Ca(NO_3)_2 + N$.[8] The action with KI resulting in the formation of I_2 is claimed to be a delicate test for N_2O_4.[9]

Nitrogen pentoxide, N_2O_5, is obtained by the dehydration of HNO_3.[10] It is a powerful oxidizing agent.[11]

Hydroxylamine,[12] NH_2OH, when pure is a white, crystalline solid, melting at 33° and boiling at 58° under 22 mm. pressure. It is very unstable, decomposing slowly at room temperature. An aqueous solution reacts alkaline and soon decomposes: $3\ NH_2OH \rightarrow$

[1] Cf. Pierce, *J. Phys. Ch.*, **33**, 22 (1929).

[2] Hüfner, *Z. physik. Ch.*, **59**, 416 (1907), *C.A.* **2**, 973.

[3] Baume and Robert, *Compt. rend.*, **169**, 968–70 (1919), *C.A.* **14**, 701, have considered the properties of pure N_2O_3.

[4] Baker and Baker, *J. Ch. Soc.*, **91**, 1862 (1907).

[5] Cf. Wieland, *Ber.*, **54B**, 1776–84 (1921), *C.A.* **16**, 212. For the structure of NO_2 see: Perkins, *Philippine J. Sci.*, **19**, 729 (1922), *C.A.* **16**, 2254; Oddo, *Gazz. ch. ital.*, **45, I,** 413–43 (1915), *C.A.* **10**, 567.

[6] Latimer and Hildebrand, p. 158.

[7] Park and Partington, *J. Ch. Soc.*, **125**, 74 (1924).

[8] Oswald, *Ann. ch.*, [9] **1**, 32 (1914).

[9] Pring, *Ch. News*, **109**, 73–5 (1914).

[10] Daniels and Bright, *J. Am. Ch. Soc.*, **42**, 1131 (1920).

[11] For preparation and properties see Russ and Pokorny, *Monatsh.*, **34**, 1027, 1051 (1913).

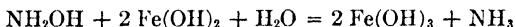
[12] The two hydroxides, NO·OH(HNO_2) and NO_2OH(HNO_3) are discussed in separate sections, §231 and §232 respectively.

$N_2 + NH_3 + 2\ H_2O$. As a result, hydroxylamine is generally encountered as the hydrochloride, $NH_2OH{\cdot}HCl$, the sulfate, $2\ NH_2OH{\cdot}H_2SO_4$, or the nitrate, $NH_2OH{\cdot}HNO_3$, which are more stable although less soluble than the base itself. The preparation of NH_2OH generally involves the reduction of a more highly oxidized compound. One method well recommended is treatment of HNO_2 with H_2SO_3 to obtain $N(SO_3H)_3$, which upon hydrolysis gives NH_2OH. Another method involves the electrolysis of a cold solution of H_2SO_4 (50%) and HCl (25%) to which is slowly added HNO_3 (50%). The hydroxylamine is formed at the mercury or amalgamated lead cathode in an 80% yield.[1]

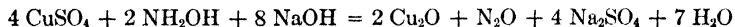
Hydroxylamine is a strong reducing agent, being readily oxidized to N_2, nitrogen oxides or HNO_2, depending upon conditions. It will also function as an oxidizing agent, especially in alkaline solutions, itself becoming NH_3. Solutions of Ag^+, Hg^{++}, Au^{+3} and Pt^{+4} are reduced by NH_2OH with formation of the corresponding metal; Cu^{++} forms Cu_2O. Ferric ion in acid solution is reduced to Fe^{++}; if boiled, the reaction may be made quantitative:

$$4\ FeCl_3 + 2\ NH_2OH = 4\ FeCl_2 + N_2O + H_2O + 4\ HCl$$

In an alkaline solution $Fe(OH)_2$ is oxidized by hydroxylamine to $Fe(OH)_3$:

$$NH_2OH + 2\ Fe(OH)_2 + H_2O = 2\ Fe(OH)_3 + NH_3$$

In Na_2CO_3 solution NH_2OH may be quantitatively oxidized by iodine.

Fehling's solution may be used for the detection of NH_2OH, the test being sensitive to one part in 100,000:[2]

$$4\ CuSO_4 + 2\ NH_2OH + 8\ NaOH = 2\ Cu_2O + N_2O + 4\ Na_2SO_4 + 7\ H_2O$$

If a mixture of NH_2OH, $(NH_4)_2S_x$ and NH_3 is treated with a few drops of $MnSO_4$ an evanescent purple color develops.[3] This is also a delicate test. Hydroxylamine may be determined by oxidation with Fe^{+3} and titration of the Fe^{++} formed with $KMnO_4$.[4]

5. Solubility. — Nitrogen is practically insoluble in all known liquids.

6. Reactions. — At ordinary temperatures nitrogen does not react with other substances. Compounds of nitrogen with the halogens are very explosive. Nitrogen chloride, NCl_3, is obtained as an oily liquid by treating NH_4Cl with Cl_2. Nitrogen iodide, $N_2H_3I_3$ or $NH_3{\cdot}NI_3$, is obtained in the form of colorless crystals by dissolving iodine in NH_4OH.

7. Ignition. — At elevated temperatures nitrogen combines with various metals to form nitrides such as Li_3N, Ag_3N, Mg_3N_2, etc. It is chiefly because of the same type of action with tantalum that the latter cannot be used in place of platinum for crucibles.

8. Detection. — Nitrogen is more easily detected by the nature of its compounds than by the properties of the free element.

9. Determination.[5] — Nitrogen, as a gas, may be determined by measuring the residual gas volume after the removal of other gases. In compounds nitrogen may be liberated by burning the compound mixed with copper oxide in an atmosphere of CO_2. The gas obtained is purified by washing with a solution of KOH and then measured.[6] For a majority of nitrogen compounds the Kjeldahl method[7] is much simpler. This involves decomposition of the sample with H_2SO_4 under suitable conditions[8] to convert the nitrogen into $(NH_4)_2SO_4$. An excess of NaOH is added to the residue and the NH_3 liberated is distilled over into standard acid, the excess being determined subsequently by titra-

[1] Tafel, *Z. anorg. allgem. Ch.*, **31**, 289 (1902).

[2] Jones and Carpenter, *J. Ch. Soc.*, **83**, 1394 (1903).

[3] Fischer, *Ch. Ztg.*, **47**, 401 (1923).

[4] Bray, *et al.*, *J. Am. Ch. Soc.*, **41**, 136 (1919).

[5] Cf. Hillebrand and Lundell, p. 633, *et seq.*

[6] Dumas, *Ann. ch. phys.*, **2**, 198 (1831).

[7] Kjeldahl, *Z. anal. Ch.*, **22**, 266 (1883). Cf. Anderson and Jensen, *Z. anal. Ch.*, **67**, 427–48 (1926), *C.A.* **20**, 1367.

[8] There is no universal method, different compounds requiring different decomposition mixtures. Some require the addition of HgO and K_2SO_4; others work better with $Hg^{\circ} + Na_2SO_4$, etc.

tion. A simple method for the determination of nitrogen in nitrates involves decomposition of the sample with H_2SO_4 in the presence of Hg° to give NO, the volume of which is measured.[1]

§231. Nitrous Acid. HNO_2

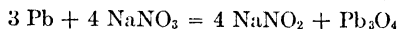
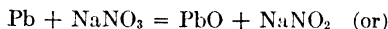
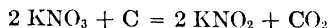
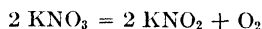
1. Physical Properties. — Nitrous acid has not been isolated in the free state. Its aqueous solution, freshly prepared by adding nitrous anhydride, N_2O_3, to cold water, is blue but the color soon fades and brown fumes are evolved: $3\ HNO_2 = HNO_3 + 2\ NO + H_2O$.[2] Nitrous acid is a moderately strong acid.[3] Its salts hydrolyze in water sufficiently to give a slightly alkaline reaction which increases with the age of the solution.

3. Preparation. — Nitrous acid may be prepared by adding H_2SO_4 to a solution of $Ba(NO_2)_2$.[4] Nitrites of the alkalis are readily obtained by heating the corresponding nitrate alone or with a reducing agent:

$$2\ KNO_3 = 2\ KNO_2 + O_2$$

$$2\ KNO_3 + C = 2\ KNO_2 + CO_2$$

$$Pb + NaNO_3 = PbO + NaNO_2 \quad \text{(or)}$$

$$3\ Pb + 4\ NaNO_3 = 4\ NaNO_2 + Pb_3O_4$$

5. Solubilities. — Silver nitrite is only slightly soluble, the other normal nitrites are soluble but many basic nitrites as well as some complex compounds, e.g., $K_3Co(NO_2)_6$, are insoluble.

6. Reactions. — Nitrous acid readily acts as an oxidizing or a reducing agent[5] but forms only a few insoluble compounds. Silver nitrite,[6] $AgNO_2$, white, is precipitated upon adding NO_2^- to a solution of $AgNO_3$. Yellow potassium cobaltinitrite forms in an acetic acid solution upon adding K^+ to $Co(NO_2)_3^{-3}$ (p. 419). Several other complex nitrites (Cr^{+3}, Cu^{++}, etc.) are known but they are of minor importance. As an oxidant HNO_2 usually forms NO, but under certain conditions, N_2O, N and even NH_3 may be obtained. It reacts with Sn^{++} to give Sn^{+4}, with Fe^{++} in acid solution to produce Fe^{+3} ($2\ FeSO_4 + H_2SO_4 + 2\ HNO_2 = Fe_2(SO_4)_3 + 2\ NO + 2\ H_2O$). In neutral or alkaline solution $Fe(OH)_2$ will quantitatively reduce nitrites to NH_3. Metallic zinc and acetic acid slowly reduce NO_2^- to NH_3, the action is rapid with Al° in NaOH.

Among the non-metals, H_2S is oxidized to S°,[7] SO_2 to SO_3,[8] KI to I_2, NH_4^+ to N_2, urea to N_2 ($2\ NO_2^- + CO(NH_2)_2 + 2\ H^+ = CO_2 + 3\ H_2O + 2\ N_2$),[9] etc.

Nitrous acid reduces all ordinary oxidizing agents with the formation of HNO_3; $Cr_2O_7^{--}$ becomes Cr^{+3}; $KMnO_4$ forms Mn^{++} ($2\ KMnO_4 + 5\ HNO_2 + 3\ H_2SO_4 = K_2SO_4 + 2\ MnSO_4 + 5\ HNO_3 + 3\ H_2O$). BrO_3^-, ClO_3^- and IO_3^- produce the free halogens and apparently decrease in activity in the order mentioned.[10] $NaNO_2$ in $NaHCO_3$ solution reacts with ClO^- to form Cl^- and NO_3^-. Sulfuric acid, concentrated or dilute, decomposes NO_2^- with evolution of NO_2 and NO.

[1] The Du Pont nitrometer is convenient for this purpose.

[2] Klemenc and Pollak, *Z. physik. Ch.*, **101**, 150 (1922). Cf. Knox and Reid, *J. Soc. Ch. Ind.*, **38**, 105–8T (1919); Rây, *et al.*, *J. Ch. Soc.*, **111**, 413–7 (1917).

[3] Klemenc and Hayek, *Monatsh.*, **53**, 407 (1929), *C.A.* **24**, 542, state that the dissociation constant at 12.5° is 0.0_346.

[4] Rây, *et al.*, *loc. cit.*

[5] Divers, *J. Ch. Soc. (Proc.)*, **23**, 269 (1907), believes that nitrites as such do not oxidize. When oxidation occurs it is HNO_2, formed by hydrolysis, that is active.

[6] Ostwald, *Ann. ch.*, [9] **1**, 32–112 (1914), *C.A.* **8**, 1927.

[7] Cf. Bagster, *J. Ch. Soc.*, **1928**, 2631–43.

[8] There is no action between nitrite and normal sulfites; H_2SO_3 forms initially $HSO_3 \cdot NO$, then $H_2N_2O_2$, NH_2OH and ultimately NH_3.

[9] These last two reactions are often used to remove NO_2^- from solution.

[10] Cf. Kurtenacker (*C.A.* **16**, 3421).

7. Ignition. — In general, nitrites are changed to oxides. With KNO_2 or $NaNO_2$ a white heat is required; with the nitrites of Ag, Hg, Au and Pt the free metal is produced.

8. Detection. — (*a*) A brown ring is formed by Fe^{++} and a nitrite when acidified with acetic acid. Nitrates require a stronger acid. (*b*) A mixture of a nitrite and KI liberates I_2 on addition of acetic acid. Using starch to detect the iodine, this test will reveal one part of NO_2^- in ten million of solution. Many other ions interfere. (*c*) A sensitive test for NO_2^- involves the appearance of a red color when $HC_2H_3O_2$, $K_2C_2O_4$, $MnSO_4$ and H_2O_2 are added, in the order given, to 2 cc. of a NO_2^- solution.[1] (*d*) If a nitrite is added to an almost colorless solution of potassium ferrocyanide acidified with $HC_2H_3O_2$, a greenish-yellow color will be obtained (distinction from NO_3^-). The test is sensitive to 1 : 600,000. (*e*) A large number of organic dyes and intermediates have been suggested for the detection of NO_2^-. (α) Diphenylamine gives a blue color with NO_2^-, the intensity being proportional to the amount of nitrite present.[2] (β) Safranine T, in the presence of H_2SO_4, gives a deep blue color with one part NO_2^- in five million of solution.[3] (γ) Sulfanilic acid with α-naphthylamine forms a deep red solution when treated with a nitrite.[4] (δ) Magenta, when used in conjunction with α-naphthol or α-naphthylamine, is possibly the most sensitive reagent for NO_2^-.[5, 6]

9. Determination. — *Gravimetrically*, nitrite may be determined by treatment with $AgBrO_3$. The AgBr formed is dried and weighed as such.[7] *Volumetrically*, (*a*) nitrite may be treated with KI and the iodine liberated titrated with thiosulfate. (*b*) Nitrite may be converted to NH_3 by $Fe(OH)_2$ in NaOH solution. The NH_3 is removed by distillation, absorbed in excess acid and the excess ascertained by titration. *Colorimetrically*, nitrite may be determined by treatment with an organic dye, the color obtained being compared with that of a known sample.[8] *Gasometrically*, HNO_2 may be converted to N_2 and the volume measured ($4\ HNO_2 + 2\ CH_2O = 3\ CO_2 + 2\ N_2 + 5\ H_2O$).[9]

§232. Nitric Acid. HNO_3

1. Physical Properties. — Pure nitric acid exists below $-41°$ in the form of white crystals, which on melting decompose slightly to N_2O_5 and H_2O. If the N_2O_5 is removed by means of an inert gas the liquid remaining contains 98.7% HNO_3.[10] The boiling point of pure HNO_3 is about 86° at atmospheric pressure.[11] If a dilute solution is boiled it becomes stronger; a concentrated solution when boiled becomes weaker. In either case a constant boiling acid is obtained at 120.5° having a specific gravity of 1.42 and containing about 70% HNO_3.[12] This is the acid usually encountered commercially. The so-

[1] Hermans, *Pharm. Weekblad*, **57**, 462 (1920), *C.A.* **14**, 3039.

[2] Tassily and Savoire, *Bull. soc. ch.*, **39**, 1755–9 (1926), *C.A.* **21**, 1075. Cf. Withers and Ray, *J. Am. Ch. Soc.*, **33**, 708–11 (1911); Tillmans and Sutthoff, *Z. anal. Ch.*, **50**, 473–95 (1911), *C.A.* **5**, 3211.

[3] Eegriwe, *Z. anal. Ch.*, **69**, 382 (1926), *C.A.* **21**, 873.

[4] Lunge, *Z. angew. Ch.*, **2**, 666 (1889).

[5] Dubský and Okáč, *Z. anal. Ch.*, **75**, 92–111 (1928), *C.A.* **23**, 63; *Rec. trav. ch.*, **46**, 296 (1927), came to this conclusion after studying over 100 dyestuffs.

[6] For a number of other organic reagents for NO_2^-, see Mellor, VIII, 465–6; Gutzeit, *Helv. Ch. Acta*, **12**, 713–40 (1929), *C.A.* **23**, 4645.

[7] Busvold, *Ch. Ztg.*, **38**, 28 (1914), **39**, 214 (1915).

[8] Letts and Rea, *Analyst*, **39**, 350 (1914), *C.A.* **8**, 3402; Germuth, *Ind. Eng. Ch., Anal. Ed.*, **1**, 28–9 (1929).

[9] Vanino and Schinner, *Z. anal. Ch.*, **52**, 21 (1913), *C.A.* **7**, 1461.

[10] Küster and Münch, *Z. anorg. allgem. Ch.*, **43**, 350 (1905).

[11] Roscoe, *J. Ch. Soc.*, **13**, 146 (1861).

[12] At 760 mm. a mean composition of 68.18% acid and a boiling temperature of 121.70° were obtained by Creighton and Githens, *J. Franklin Inst.*, **179**, 161–9 (1915), *C.A.* **9**, 744.

called fuming acid is a solution of HNO_3 containing a variable amount of NO_2; it has a specific gravity of about 1.50, and should be kept in a cool, dark place to avoid decomposition.[1,2]

2. Occurrence. — Nitrates of K, Na, NH_4, Ca, Mg and of a few other metals are found native. The most abundant supply comes from Chile and Bolivia as sodium nitrate, "Chile saltpeter."

4. Preparation. — Commercially, HNO_3 is prepared by treating Chile saltpeter with H_2SO_4 and heating to 130° whereupon HNO_3 distils off leaving a residue of "nitre cake," $NaHSO_4$. Nitric acid is also obtained in some of the processes for the fixation of atmospheric nitrogen. In the "arc" process N and O combine when subjected to the heat of an electric arc. The nitrogen oxides formed are absorbed in H_2O from which solution HNO_3 is prepared. In the "ammonia" process NH_3 is oxidized to NO_3^- by means of a catalyst.

Nitrates may be made (*a*) by dissolving the metal in HNO_3 except in the case of Au, Pt, Al and Cr, which are not attacked by that acid; also, Sb forms Sb_2O_5, arsenic gives H_3AsO_4, and with excess of hot HNO_3 tin forms β-stannic acid (p. 225); (*b*) by adding HNO_3 to the oxides, hydroxides or carbonates. All of the known nitrates can be made in this manner. (*c*) Upon long boiling the chlorides of all ordinary metals are completely decomposed by HNO_3, no chlorine remaining. The exceptions to this generalization are the chlorides of Hg, Ag, Au and Pt, which are not attacked, and the chlorides of Sn and Sb, which are changed to oxides.

5. Solubilities. — All normal nitrates are soluble in water. A few are decomposed by this solvent, e.g., $Bi(NO_3)_3 + H_2O = BiONO_3 + 2\,HNO_3$. Practically all nitrates are less soluble in HNO_3 than in H_2O, e.g., Cd, Pb, Ba, etc. The barium salt is only slightly soluble in acid of density 1.42.

6. Reactions. — *A.* **With metals and their compounds.** — Nitric acid is a powerful oxidizer, but unless warm acts more slowly than chlorine. If the acid is concentrated, in excess and hot, the product is usually entirely nitric oxide, NO.[3] Excess of the reductant, a low temperature and dilute solution favor the production of compounds in which the nitrogen has a lower valence. Nascent hydrogen usually forms NH_3, always the ultimate product if the hydrogen is formed in an alkaline system. The only metal that reacts with HNO_3 to give H_2 is magnesium. Even in this case the acid must be very dilute. Many metals are passive in concentrated HNO_3 but dissolve readily in a dilute solution. It is claimed by some workers that the presence of HNO_2 is necessary to start the reaction.[4] Other substances as $KMnO_4$, $KClO_3$, etc., have also been found to exert a catalytic effect.[5,6]

[1] For the action of light on HNO_3, see: Reynolds and Taylor, *J. Ch. Soc.*, **101**, 131 (1912).

[2] For the constitution of HNO_3, see: Hantzsch, *Ber.*, **58B**, 941 (1925).

[3] Rapidly oxidized to NO_2.

[4] A recent paper on this subject is by Klemenc and Klima, *Z. anorg. allgem. Ch.*, **179**, 379 (1929), *C.A.* **23**, 2871.

[5] Banerji and Dhar, *Z. anorg. allgem. Ch.*, **122**, 73–80 (1922), *C.A.* **16**, 3023.

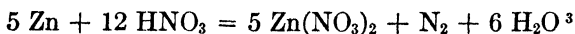
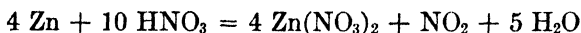
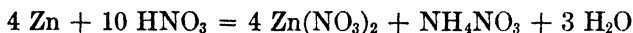
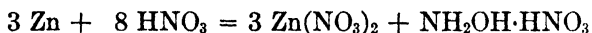
[6] For the mechanism of the action of HNO_3 on metals see Friend, VI, 1, p. 198 *et seq.*; also, Bancroft, *J. Phys. Ch.*, **28**, 475–93 (1924), who after reviewing the previous work, concludes that the action is electrolytic corrosion, the anode reaction forming nitrate, and that the products, HNO_2, $H_2N_2O_2$, NH_2OH, NH_3, NO_2, NO, N_2O_4 and N_2, are due to secondary reactions. See further: Joss, *Ibid.*, **30**, 1222–75 (1926).

Nitric acid oxidizes all ordinary metals but does not act upon chromium, aluminum,[1] gold or platinum. It forms nitrates, except in the case of Sn°, Sb° and As° (q. v.). With the following metals it forms the lower or higher valence according to the amount of HNO_3 employed: Hg, Sn, As, Sb, Fe. Copper always forms Cu^{++}, while cobalt becomes Co^{++}. The metals Cu, Ag, Hg and Bi differ from the others in their action with HNO_3 in that the main products are chiefly the nitrate and nitric oxide:[2] $3\ Cu + 8\ HNO_3 = 3\ Cu(NO_3)_2 + 2\ NO + 4\ H_2O$. Using zinc (cf. Fe, p. 316) as an example of the action with the other metals, the main products vary materially depending upon conditions and the ratio between acid and metal:

$$3\ Zn + 8\ HNO_3 = 3\ Zn(NO_3)_2 + NH_2OH{\cdot}HNO_3$$

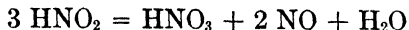
$$4\ Zn + 10\ HNO_3 = 4\ Zn(NO_3)_2 + NH_4NO_3 + 3\ H_2O$$

$$4\ Zn + 10\ HNO_3 = 4\ Zn(NO_3)_2 + NO_2 + 5\ H_2O$$

$$5\ Zn + 12\ HNO_3 = 5\ Zn(NO_3)_2 + N_2 + 6\ H_2O$$ [3]

Ferrous hydroxide (or $FeO{\cdot}H_2O$) quantitatively reduces the nitrate ion to NH_3 (cf. p. 472).

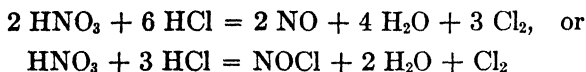
B. **With non-metals and their compounds.**

1. *Carbon* (ordinary, not graphite) becomes CO_2 if the HNO_3 is hot and concentrated.
   $H_2C_2O_4$ becomes $CO_2 + H_2O$.
   $H_4Fe(CN)_6$ is first oxidized to $H_3Fe(CN)_6$ then to hydronitroferricyanic acid.
   HCNS is oxidized, the S becoming H_2SO_4.
2. All *nitrites* are decomposed, nitrates being formed, but the HNO_3 is not reduced. The HNO_2 liberated immediately dissociates:

$$3\ HNO_2 = HNO_3 + 2\ NO + H_2O$$

3. *Phosphorus* having a valence lower than five (P°, PH_3, H_3PO_2, H_3PO_3) becomes H_3PO_4.
4. *Sulfur* becomes H_2SO_4.
   H_2S, depending upon the concentration and temperature of the HNO_3, becomes S° or H_2SO_4.
   H_2SO_3 becomes H_2SO_4.

[1] Cf. Seligman and Williams, *J. Soc. Ch. Ind.*, **35**, 665 (1916).
[2] Stansbie, *J. Soc. Ch. Ind.*, **32**, 311, 1135 (1925), **27**, 365 (1908), has determined the gaseous products resulting from the action of HNO_3 (sp. g. 1.2) on Cu°, Bi° and Ag° at 65°. One gram of Cu, upon dissolving, produced 162.3 cc. of NO, 6.7 cc. of NO_2 and 13.9 cc. of N.
[3] Friend, VI, 1, p. 199.

5. *Hydrochloric acid* reacts with HNO_3 to form aqua regia:

$$2\ HNO_3 + 6\ HCl = 2\ NO + 4\ H_2O + 3\ Cl_2, \quad \text{or}$$
$$HNO_3 + 3\ HCl = NOCl + 2\ H_2O + Cl_2$$

6. *Hydrobromic acid* becomes Br° and is not further oxidized.
7. *Hydriodic acid* is oxidized first to I° then to HIO_3. The reaction is slow unless fuming HNO_3 is used.

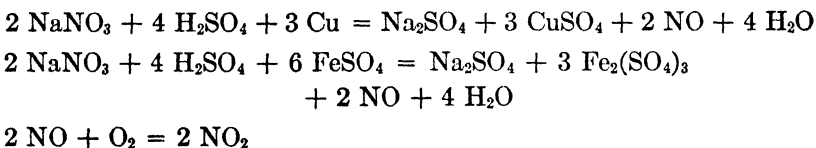
7. **Ignition.** — Nitric acid is dissociated by heat: $4\ HNO_3 = 4\ NO_2 + O_2 + 2\ H_2O$. The reaction is complete at 256°. Nitrates, as such, are non-volatile; NH_4NO_3 undergoes decomposition: $NH_4NO_3 = N_2O + 2\ H_2O$. Some nitrates, e.g., those of K and Na, are first changed to nitrites with evolution of O_2, then at an intense, white heat further changed to oxides with evolution of NO_2 as well as oxygen. As a final result of ignition the nitrates of all ordinary metals are left as oxides, except that those of Hg, Ag, Au and Pt are reduced to the free metal.

A mixture of KNO_3 and Na_2CO_3 in a state of fusion is a powerful oxidant, changing Sn^{II} to Sn^{IV}, As^{III} to As^{V}, Sb^{III} to Sb^{V}, Fe^{II} to Fe^{III}, Cr^{III} to Cr^{VI}, Mn^{II} to Mn^{VI}, sulfide to S^{VI}.

Heated on charcoal or with a cyanide, sugar, sulfur or other easily oxidized substance (as in gunpowder), nitrates are reduced with deflagration or explosion; using KCN on a platinum foil the deflagration is especially vivid. In this reaction N_2 is evolved.

8. **Detection.** — Most of the tests for the identification of nitric acid involve its reduction to a lower oxide or even to ammonia.

a. If, with concentrated H_2SO_4, a small piece of Cu° or a crystal of ferrous sulfate is added to a concentrated solution or residue of a nitrate, the mixture will give off abundant brown vapors of NO_2.

$$2\ NaNO_3 + 4\ H_2SO_4 + 3\ Cu = Na_2SO_4 + 3\ CuSO_4 + 2\ NO + 4\ H_2O$$
$$2\ NaNO_3 + 4\ H_2SO_4 + 6\ FeSO_4 = Na_2SO_4 + 3\ Fe_2(SO_4)_3 + 2\ NO + 4\ H_2O$$
$$2\ NO + O_2 = 2\ NO_2$$

b. **Brown Ring Test.** — If, in the $FeSO_4$ reaction, the nitric oxide is liberated in a cold solution containing excess $FeSO_4$ and H_2SO_4, instead of being evolved the NO combines with the ferrous salt to form a brown liquid, $FeSO_4{\cdot}NO$,[1] readily decomposed by heat. $2\ NaNO_3 + 4\ H_2SO_4 + 8\ FeSO_4 = 2\ FeSO_4{\cdot}NO + 3\ Fe_2(SO_4)_3 + Na_2SO_4 + 4\ H_2O$. This so-called "brown ring" test is sensitive to about one part of nitrate in ten thousand of solution.[2] A number of ions interfere, as I^-, Br^-, $Cr_2O_7^{--}$, ClO_3^-, etc.; furthermore, the solution to be tested must not be deeply colored.

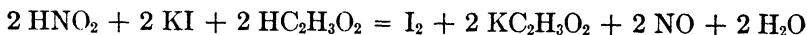
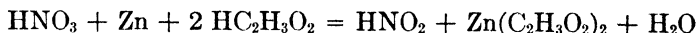
[1] Manchot and Haunschild, *Z. anorg. allgem. Ch.*, **140**, 22–6 (1924), *C.A.* **19**, 1083. Manchot has published a number of papers on this subject.

[2] Wagner, *Z. anal. Ch.*, **20**, 329 (1881). Cf. Hahn and Jaeger, *Ber.*, **58B**, 2335, 2340 (1925).

c. **Ammonia Test.** — A solution of NO_3^- treated with NaOH and Al° will evolve NH_3 which may be detected by means of litmus paper, Nessler's reagent or $MnSO_4 + H_2O_2$ (p. 425). Ammonium ions must be removed by boiling the solution with NaOH before addition of the metal. Nothing else interferes with this test. Action is delayed, however, by strong oxidants as ClO_3^-, $Cr_2O_7^{--}$, etc.

d. **Nitrite Test.** — A solution of NO_3^- is treated with Zn° and acetic acid. At short intervals a portion of the liquid is decanted, a drop of KI added followed by a drop of CCl_4 to detect any iodine liberated. Other oxidants as ClO_3^-, BrO_3^-, IO_3^-, AsO_4^{-3}, etc., are reduced before reduction of the HNO_3 begins. The test will detect one part of nitrate in one hundred thousand of solution:[1]

$$HNO_3 + Zn + 2\ HC_2H_3O_2 = HNO_2 + Zn(C_2H_3O_2)_2 + H_2O$$

$$2\ HNO_2 + 2\ KI + 2\ HC_2H_3O_2 = I_2 + 2\ KC_2H_3O_2 + 2\ NO + 2\ H_2O$$

Other means of making the nascent hydrogen are sometimes preferred, e.g., Cd° + $HC_2H_3O_2$, sodium amalgam, Al° + NaOH, Mg° + H_3PO_4, etc. It should be noted that in any case the nitrite is but an intermediate stage in the reduction of the nitrate. If the reaction period is too short insufficient NO_2^- will have been formed; if too long, the nitrogen will have been reduced beyond the nitrite state. Hence the necessity for removal of portions at short intervals.

e. **Diphenylamine Test.** — Addition of about 3 cc. of the sample to 2 cc.[2] of diphenylamine, $(C_6H_5)_2NH$, dissolved in H_2SO_4, results in the production of a blue color if an oxidant[3] is present. In the absence of all but NO_3^- the procedure becomes a test for that ion. The test is very delicate. *Diphenylbenzidine* gives a more pronounced blue-violet color and is more sensitive.[4]

f. **Brucine,** in concentrated H_2SO_4, treated (on a white porcelain surface) with even a trace of NO_3^-, gives a deep red color soon fading to reddish yellow. If dilute $SnCl_2$ is added a fine red-violet color appears. Chlorates interfere.

g. A little **pyrogallol** is dissolved in the liquid to be tested (less than 1 mg./cc.) and ten drops of concentrated H_2SO_4 are poured down the side of the test tube to form two layers. At the surface of contact a brown or yellow coloration appears if NO_3^- is present.[5]

[1] Wagner, *Z. anal. Ch.*, **20**, 329 (1881).

[2] When applying this test the concentration of each material is important. Weinhagen, *J. Am. Ch. Soc.*, **43**, 685 (1921).

[3] For details about the color obtained with a number of reagents see: Ekkert, *Pharm. Zentralhalle*, **66**, 649 (1925), *C.A.* **20**, 158. Cf. Lutschinsky, *Ch. Ztg.*, **36**, 1239 (1912), *C.A.* **7**, 956.

[4] Riehm, *Z. anal. Ch.*, **81**, 439–47 (1930), *C.A.* **25**, 55.

[5] Cf. De Nardo, *Compt. rend.*, **188**, 563 (1929), *C.A.* **23**, 2123.

h. Various modifications of tests for nitrite involving organic dyes have been suggested for the detection of nitrate. The NO_3^- may be reduced to HNO_2 by lead formate and the HNO_2 detected by means of the red color obtained with sulfanilic acid and α-naphthylamine in acetic acid. A good test can be obtained with 1 mg. of KNO_3 in a liter of solution.[1, 2]

9. Determination. — *Gravimetrically,* nitrate ion may be precipitated with "nitron," dried at 110° and weighed as nitron nitrate. Many other ions interfere.[3] *Volumetrically,* nitrates may be reduced to NH_3, which is absorbed in standardized acid, the excess being titrated with an alkali.[4] For the colorimetric determination of small amounts of nitrate De Nardo[5] has suggested the use of pyrogallolsulfonic acid. Smith[6] has advocated the use of diphenylamine or diphenylbenzidine. *Gasometrically,* a nitrate may be reduced to NO by $Hg^0 + H_2SO_4$ and the volume of gas measured in a nitrometer, the Du Pont assembly being convenient for this determination.

§233. Oxygen (and Hydrogen Peroxide). (Gr. *oxus genes* = acid former). O = 16.0000. Atomic No. 8. Valence 2. Discovered by Scheele in 1771.[7]

1. Physical Properties. — Oxygen is a colorless, odorless gas. Its density under standard conditions is 1.42901 g./l.;[8] critical temperature, 118°; critical pressure, 49.3 atmospheres.[9] The melting point of solid oxygen is − 219°;[10] the boiling point of the liquid is −182.9°. The density of solid oxygen is 1.4256 at −252.5°;[11] of liquid oxygen 1.1700 at −195°.[12] The liquid is strongly magnetic. Oxygen is slightly soluble in water. Molten silver dissolves about ten volumes of the gas, giving it up on cooling (spitting of silver). In an atmosphere of oxygen a glowing splinter bursts into a flame; phosphorus burns with vivid incandescence; an iron watch spring, heated with burning sulfur, ignites and burns with marked brilliancy. Oxygen is the most negative of all the elements except fluorine; it combines directly or indirectly[13] with all the elements except fluorine[14] and the rarer gases of the air. The combination of oxygen with other substances is termed oxidation or combustion depending upon the rate of the reaction.

[1] Hahn and Jaeger, *Ber.*, **58B**, 2335 (1925), *C.A.* **20**, 158.

[2] For other tests see: Gutzeit, *Helv. Ch. Acta*, **12**, 713–40 (1929), *C.A.* **23**, 4645; Vági, *Z. anal. Ch.*, **66**, 101 (1925); Ekkert, *Pharm. Zentralhalle*, **66**, 733 (1925).

[3] Busch, *Ber.*, **38**, 861 (1905); **39**, 1401 (1906).

[4] Devarda, *Ch. Ztg.*, **16**, 1952 (1892); *Z. anal. Ch.*, **33**, 113 (1894); Harrison, *J. Biol. Ch.*, **46**, 53 (1921), *C.A.* **15**, 1473.

[5] De Nardo, *Compt. rend.*, **188**, 563 (1929), *C.A.* **23**, 2122.

[6] Smith, *Z. anal. Ch.*, **56**, 28–42 (1917), *C.A.* **11**, 2759.

[7] Abegg, IV, 1, 1, p. 11 (1927). This volume contains a good discussion of oxygen and ozone, also on pp. 101–113 a bibliography of 523 references covering the literature down to December, 1924.

[8] Baxter and Starkweather, *Proc. Nat. Acad. Sci.*, **10**, 479 (1924). Cf. Moles, *J. ch. phys.*, **19**, 100–20 (1921), *C.A.* **16**, 3779. Morley's mean value is 1.42900, *Z. physik. Ch.*, **20**, 68 (1896).

[9] Cardoso, *J. ch. phys.*, **13**, 312 (1915).

[10] Estreicher, *Z. physik. Ch.*, **85**, 432 (1913), *C.A.* **8**, 599.

[11] Dewar, *Proc. Roy. Soc.* (*London*), **85A**, 589 (1911).

[12] *Idem*, **73**, 251 (1904).

[13] There are only a few in this group; the halogens, Ag, Au, Pt.

[14] Recent work of Dennis and Rochow, *J. Am. Ch. Soc.*, **54**, 832 (1932) would include fluorine.

The temperature at which combustion takes place, i.e., the kindling point, varies greatly depending on the fuel.

2. Occurrence. — The rocks, clay, etc., constituting the main part of the earth's crust contain 44%–48% of oxygen; water contains about 89% and the air about 21%, making a grand average of 47.75% for all three.[1]

3. Preparation. — Oxygen may be prepared (*a*) by heating $KClO_3$ to 240° in a closed retort in the presence of MnO_2[2] or Fe_2O_3. If the chlorate is heated alone, a higher temperature (350°) is required and the gas may be given off with explosive violence. (*b*) BaO is heated in air at 600° then the pressure is reduced to 4 mm. and the oxygen pumped off: $2\ BaO + O_2 \rightleftarrows 2\ BaO_2$. This process, once used commercially, is now obsolete. (*c*) Warming a solution of bleaching powder[3] containing a small amount of freshly prepared cobaltic oxide results in a smooth evolution of oxygen. The essential reaction probably is: $Ca(ClO)_2 \rightleftarrows CaCl_2 + O_2$, the Co_2O_3 acting as a catalyst. (*d*) Fused Na_2O_2 will give a steady stream of O_2 if H_2O is added dropwise. A modification of this idea is to warm a mixture of Na_2O_2 and Glauber's salt.[4] (*e*) The electrolysis of water in the presence of an alkali gives oxygen, 97% pure. (*f*) Probably the most important commercial process is the fractional distillation of liquid air. Nitrogen boils at − 195.7°, oxygen at − 182.9°, hence on warming liquid air the N_2 boils off first leaving a residue rich in oxygen. With sufficient care a high-grade product is obtainable.

4. Hydrides, Oxides and Acids. — The hydride, H_2O, will not be discussed here. *Ozone*, O_3, was first noticed by Van Marum in 1785 as a peculiar smelling gas formed during the discharge of a static electricity machine. Schönbein named the gas "ozone" and noted its powerful oxidizing properties. It is said to be an ever-present ingredient of the air; present much more in the country and near the seashore than in the air of cities. Ozone is always mixed with ordinary oxygen — of which it is an allotropic form — partly due to a dissociation of the ozone molecule, which is stable only at low temperatures. Ozone is a blue gas, its density is 2.1445 g./l. at S.T.P.; critical temperature, − 5°; critical pressure 64.8 atmospheres; melting point of solid O_3, − 250°; boiling point, − 112.3°.[5] Ozone is prepared (*a*) by the action of the silent discharge on oxygen; at − 78° the yield of O_3 is 11%; at − 194° the conversion is practically quantitative;[6] (*b*) by the electrolysis of a 15% solution of H_2SO_4 using platinum electrodes;[7] (*c*) by treating liquid air with ultraviolet light. A number of substances decompose ozone without being changed themselves, e.g., platinum black or sponge, oxide of gold, silver, iron, copper, etc. In the presence of water it is one of the most active oxidizing agents known, changing all metals except Au and Pt to the highest state of oxidation. In general the same is true of the non-metallic elements except that the hydrogen halides are oxidized to the free halogen: $2\ HI + O_3 = H_2O + I_2 + O_2$.[8] This reaction may be used both for the detection and the determination of O_3.[9] It has also been reported that ozonized oxygen produces a blue color at room temperature when passed through acetic acid, ethyl acetate, chloroform or carbon tetrachloride.[10]

Hydrogen peroxide, H_2O_2, when pure is a colorless, syrupy liquid, boiling at 69.2° under 26 mm. pressure. It solidifies, upon markedly supercooling,

[1] Clarke, U. S. Geol. Survey, Prof. Paper **127**, p. 34.

[2] Sodeau, *J. Ch. Soc.*, **81**, 1066 (1902), explains the action of MnO_2 as the alternate formation of a higher, then lower oxide.

[3] Bell, *Z. anorg. allgem. Ch.*, **82**, 145 (1913).

[4] Turner, *Am. Ch. J.*, **37**, 106 (1907).

[5] Riesenfeld and Schwab, *Ber.*, **55**, 2088–99 (1922), *C.A.* **16**, 3416. Cf. Schwab, *Z. physik. Ch.*, **110**, 599 (1924).

[6] Briner and Durand, *Compt. rend.*, **145**, 1272–4 (1907), *C.A.* **2**, 1245.

[7] Fischer and Bendixsohn, *Z. anorg. allgem. Ch.*, **61**, 13 (1909).

[8] Cf. Strecker and Thienemann, *Ber.*, **53**, 2096–2113 (1920), *C.A.* **15**, 480; Harries, *Z. anorg. allgem. Ch.*, **99**, 196 (1917); Riesenfeld and Bencker, *Z. anorg. allgem. Ch.*, **98**, 167 (1916); Yamauchi, *Am. Ch. J.*, **49**, 55–68 (1913).

[9] Yamauchi, *loc. cit.*

[10] Fischer and Tropsch, *Ber.*, **50**, 765 (1917).

to melt at − 2°. It has a density of 1.458 at 0°.[1] It is volatile in the air, readily explosive, irritating to the skin and reacts strongly acid. H_2O_2 contains more oxygen than any other compound, one-half of the oxygen being available, the other half remaining with the hydrogen as H_2O. Because of the easy liberation of the oxygen from H_2O_2 either by warming or the use of a catalyst — a small amount of alkali is effective — it is widely used as a bleaching agent. A dilute solution, about 3%, is the commercial form.[2] It is usually stabilized by the addition of a small amount of acetanilid (0.002%) and an acid.[3]

The preparation of H_2O_2 is usually effected by treatment of BaO_2 with H_2SO_4, the precipitated $BaSO_4$ being removed by filtration. The BaO_2 is obtained as indicated above (3). Sodium peroxide, Na_2O_2, is formed by heating Na° in air or oxygen. Hydrogen peroxide is miscible with water in all proportions; Na_2O_2 is readily soluble with the generation of much heat.

Hydrogen peroxide usually acts[4] as a powerful oxidizing agent[5] especially in alkaline solution, half of its oxygen being involved. Under certain conditions, however, it acts as a strong reducing agent. Some substances decompose H_2O_2 into H_2O and O_2 without changing the substance employed, e.g., Au, Ag, Pt, MnO_2, charcoal, etc. Many metals are oxidized to the highest state, e.g., Fe, Tl, As, Mo, etc.; Au and Pt are not attacked; Pb°, Hg°, Ag°, Bi° and Cu° are dissolved by glacial acetic acid containing H_2O_2;[6] Bi^{+3} fused with Na_2O_2 becomes Bi^{+5}; Cr^{+3} and Mn^{++}, treated with Na_2O_2, become CrO_4^{--} and MnO_2 respectively. As examples of the reducing action of H_2O_2, Ag_2O, HgO and Au_2O_3 are changed to the metal with liberation of oxygen; Cu^{++} in alkaline solution (Fehling's solution) becomes Cu_2O; MnO_4^- in acid solution becomes Mn^{++}. Among the non-metals H_2O_2 reacts with oxalic acid to give CO_2; $Fe(CN)_6^{-4}$ becomes $Fe(CN)_6^{-3}$; in alkaline solution the reverse action takes place: $2\,K_3Fe(CN)_6 + 2\,KOH + H_2O_2 = 2\,K_4Fe(CN)_6 + 2\,H_2O + O_2$; H_3PO_2 forms H_3PO_4; sulfides and sulfites become sulfates, particularly in alkaline solution; thiosulfates forms tetrathionates initially: $2\,Na_2S_2O_3 + H_2O_2 =$

[1] Cf. Maass and Hatcher, *J. Am. Ch. Soc.*, **42**, 2548–69 (1920); Maass and Hiebert, *Ibid.*, **46**, 290, 2693 (1924). Concerning the structure of H_2O_2 and the mechanism of its reactions, see Raikow, *Z. anorg. allgem. Ch.*, **168**, 297 (1928), *C.A.* **22**, 1921.

[2] "Perhydrol" is 30% H_2O_2 yielding on decomposition 100 times its volume of O_2. It is made by adding Na_2O_2 to ice-cold 20% H_2SO_4 and distilling the mixture. "Hyperol" is a compound of H_2O_2 and urea containing a little citric acid as a stabilizer. It may be used in place of H_2O_2, is quite stable and easily handled (Milbauer, *Ch. Ztg.*, **35**, 871 (1911), *C.A.* **5**, 3391).

[3] Jensen, (*C.A.* **14**, 2896); Walton and Judd, *Z. physik. Ch.*, **83**, 315 (1913). A study of the instability of H_2O_2 has been made by Lemoine, *J. ch. phys.*, **12**, 1–57 (1914), *C.A.* **9**, 401; Fischer, *Pharm. Zentralhalle*, **48**, 57, 79 (1907).

[4] For the reaction of peroxides with metals see part 6c under the individual elements.

[5] Fe^{++} markedly accelerates oxidation by H_2O_2. Mummery, *J. Soc. Ch. Ind.*, **32**, 889 (1913), *C.A.* **8**, 284.

[6] Cf. Salkowski, *Ch. Ztg.*, **40**, 448 (1916), *C.A.* **10**, 2559.

$Na_2S_4O_6 + 2\,NaOH$, then the reaction becomes more complicated;[1] concentrated H_2SO_4 forms H_2SO_5 (Caro's acid); ammonium persulfate undergoes complete decomposition, both N_2 and O_2 being liberated.[2] Reactions with the halogen compounds depend largely on conditions. The halides may be oxidized to the free halogens and, conversely, free halogens may be reduced to the halides.[3] If $Ca(OH)_2$ and I_2 are treated with H_2O_2 an iodide and free oxygen are formed: $Ca(OH)_2 + I_2 + H_2O_2 = CaI_2 + O_2 + 2\,H_2O$.[4] Periodic acid is reduced by H_2O_2 to iodic acid; in dilute solution the reduction is to iodine.[5] Sodium peroxide is occasionally used in the fused state as a powerful oxidant for the decomposition of refractory materials, e.g., chromite, bauxite, etc.

Many tests for a peroxide have been suggested. Among the best of these are: (*a*) the formation of blue perchromic acid with cold $Cr_2O_7^{--}$; (*b*) the appearance of yellow pertitanic acid with $Ti(SO_4)_2$; (*c*) the formation of blue starch-iodide with KI and starch; (*d*) the separation of a gray precipitate when a few drops of H_2O_2 in 100 cc. of H_2O are treated with $Ag(NH_3)_2NO_3$.[6] The quantitative determination of H_2O_2 is effected by (*a*) titration with $KMnO_4$ in acid solution; (*b*) reaction with KI in H_2SO_4 solution and titration of the liberated iodine with $Na_2S_2O_3$.

6. Reactions. — Pure, moist oxygen not under pressure may be breathed for some time without injury. The compressed gas (3.5 or more atmospheres) causes convulsions.

At varying temperatures oxygen combines directly with all metals except Ag, Au and Pt, and with these it may be made to combine indirectly. It unites with all non-metals except fluorine[7] and the rarer gases of the atmosphere, the combination occurring directly, at high temperatures, except with Cl, Br and I, which require the intervention of a third substance.

7. Ignition. — Most elements, when ignited in oxygen, readily combine with it. Some lower oxides form higher oxides, and certain ores evolve O_2, forming elements or lower oxides.

8. Detection. — Free oxygen is detected by (*a*) its combination with NO to form brown NO_2; (*b*) its combination with phosphorus to give P_2O_5 in the form of a white smoke; (*c*) the fact that it will rekindle a glowing splint (N_2O is the only gas that interferes); (*d*) the deep red color produced when an alkaline solution of pyrocatechol and $FeSO_4$ is exposed to O_2 (a very delicate test).[8]

9. Determination. — Oxygen may be determined by absorption in cuprous chloride, alkaline pyrogallol or chromous chloride, the contraction in volume of the gas sample being a measure of the O_2 absorbed. In organic compounds oxygen is determined by difference.

[1] Tarugi and Vitali, *Gazz. ch. ital.*, **39**, I, 418–25 (1909), *C.A.* **5**, 437.

[2] Kempf and Oehler, *Ber.*, **41**, 2576 (1908), *C.A.* **2**, 2764.

[3] Cf. Abel, *Z. physik. Ch.*, **96**, 1–179 (1920), *C.A.* **15**, 199.

[4] Broeksmit, *Pharm. Weekblad*, **54**, 1373 (1917), *C.A.* **12**, 338. Cf. Auger, *Compt. rend.*, **152**, 712 (1911), *C.A.* **5**, 1885.

[5] Many per-acids are considered to be derivatives of H_2O_2 but a discussion of these compounds is beyond the scope of this book. For an interesting table of per-acids, see: Caven and Landers, p. 309.

[6] Sobbe, *Ch. Ztg.*, **35**, 898 (1911), *C.A.* **5**, 3774. Cf. Margosches, *Ch. Ztg.*, **35**, 955 (1911).

[7] Cf. Dennis and Rochow, *loc. cit.*

[8] Binder and Weinland, *Ber.*, **46**, 255 (1913), *C.A.* **7**, 1459.

§234. Fluorine (L. *fluor* = flow). F = 19.00. Atomic No. 9. Valence 1. Discovered by Scheele in 1771.

Fluorine,[1] in several of its properties, appears as the first member of the halogen series of elements; in some characteristics, however, it is distinctly at variance with the other elements of the group. At room temperature fluorine is a colorless gas, so active that it is kept in the free state only with difficulty. It can be solidified, melting point, −233°; boiling point, − 187° at atmospheric pressure; density, 1.14 at the boiling point. It occurs chiefly as fluorspar, CaF_2, and as cryolite, Na_3AlF_6. Fluorine is not obtainable by the reactions ordinarily used for the preparation of halogens. It was first isolated by Moissan (1886), who, using apparatus made almost entirely of platinum, electrolyzed potassium fluoride dissolved in anhydrous hydrofluoric acid. Fluorine is now prepared by conducting the electrolysis in a copper vessel equipped with graphite electrodes. Another method involves the electrolysis of fused potassium fluoride.[2]

Fluorine is the most electronegative element known. It combines with hydrogen in the dark, even at − 252°, and will displace the chlorine from HCl. It instantly decomposes water with liberation of the oxygen. Apparently it forms no stable oxide.[3] It is a powerful oxidant,[4] oxidizing all metals except Au and Pt and reacting directly with all other elements except N, O,[5] Cl and the noble gases. Fluorine reacts with H_2S with explosive violence. An important characteristic of fluorine is its tendency to form polyfluorides.

Hydrofluoric acid, $(HF)_n$,[6] is a colorless, intensely corrosive gas; solidified, it melts at − 83°, boils at 19°. In the liquid state at 0° its dielectric constant is higher than that of H_2O.[7] It is readily soluble in water to form a weak acid (distinction from the other hydrogen halides) ionized in 0.1 *N* solution to the extent of about 10%.[8] A constant boiling mixture, containing 38.18% HF (± 0.10%) has been obtained at 110.8° under 732 mm. pressure.[9] Both the solution and its vapor act on the flesh with very little warning to produce burns that are painful and slow to heal.

Hydrofluoric acid is not found free in nature. It is usually prepared by treating fluorspar, CaF_2, with H_2SO_4 and distilling off the HF which is absorbed in water. The operation is carried out in lead-lined apparatus.[10]

The fluorides of the alkali metals are readily soluble in water. The solutions react alkaline to litmus and are slightly corrosive to glass. The fluorides of the alkaline earth metals (except BaF_2) are insoluble in water, of Cu, Pb, Fe^{+3}, Ba and Li slightly soluble, of Ag, Hg and Tl readily soluble (see Table 42).

[1] See especially, Gmelin, 8th ed., No. 5 (1926).

[2] Fredenhagen and Krefft, *Z. Elektroch.*, **35**, 670 (1929), *C.A.* **24**, 2032. Cf. Argo, *et al.*, *J. Phys. Ch.*, **23**, 348 (1919); Simons, *J. Am. Ch. Soc.*, **46**, 2175, 2179 (1924); Simons and Hildebrand, *Ibid.*, p. 2183. An interesting method not involving electrolysis is that depending upon the thermal decomposition of ceric fluoride or manganic fluoride: $CeF_4 + \text{heat} \rightarrow CeF_3 + F$; $MnF_3 + \text{heat} \rightarrow MnF_2 + F$.

[3] Cf. Lebeau and Damiens, *Compt. rend.*, **185**, 652 (1927), who report the gas F_2O.

[4] Fichter, *et al.*, *Helv. Ch. Acta*, **13**, 1200 (1930); **12**, 214 (1929); **9**, 467 (1926). The first article mentioned is Fichter's seventeenth on the subject. Cf. Bladergroen, *Ch. Weekblad*, **27**, 2 (1930).

[5] Compounds with N and O have been reported, e.g., NF_3, F_2O. Concerning the inertness toward chlorine, see Lebeau, *Ann. ch. phys.*, [8] **9**, 241 (1906).

[6] At room temperature and ordinary pressures gaseous HF is said to be 80% in the form of the polymer $(HF)_6$.

[7] Fredenhagen and Dahmlos, *Z. anorg. allgem. Ch.*, **178**, 272–4 (1929), *C.A.* **23**, 2614.

[8] Prideaux and Millott, *Trans. Faraday Soc.*, **25**, 579 (1929), state that at 18° the *p*H of 3.485 *N* HF is 0.430.

[9] Muehlberger, *J. Phys. Ch.*, **32**, 1888 (1928).

[10] Cf. Simons, *Ch. Reviews*, **8**, 213–35 (1931); Fredenhagen and Cadenbach, *Z. anorg. allgem. Ch.*, **178**, 289 (1929).

Unlike the other halogen hydrides HF is not a reducing acid. It is also notable in that it forms many double salts, e.g., KHF_2, KH_2F_3,[1] etc. Ag^+ or Hg_2^{++} does not form a precipitate with HF. Mercuric fluoride differs from $HgCl_2$ in that it is highly ionized and hydrolyzed. MnF_3 is the most stable of all manganic salts. If boric acid, H_3BO_3, is treated with HF in excess the product formed is HBF_4 (distinction from the other halogens). Silicic acid reacts with fluorides to form silicon fluoride, SiF_4, a gas that does not attack glass but when passed into water becomes fluosilicic acid, H_2SiF_6 (SiO_2 + 6 HF = H_2SiF_6 + 2 H_2O). This compound is soluble in water and its salts, the fluosilicates, are also soluble;[2] those of Ba, Na and K being only slightly soluble in water, less soluble in dilute alcohol. Potassium fluosilicate is precipitated translucent and gelatinous. Ammonium hydroxide precipitates silicic acid from H_2SiF_6. Upon heating fluosilicates decompose: $BaSiF_6 = BaF_2 + SiF_4$.

TABLE 42

Solubility of Some Fluorides in Water

Salt	PbF_2	CuF_2	CdF_2	AlF_3	FeF_3	NiF_2	CoF_2	MnF_2	BaF_2	SrF_2	CaF_2	MgF_2	LiF	NaF
Soly.*	0.066	0.075	0 622	0 559	0.091	4 030	1 415	0 186	0 121	0.039	0.004	0.013	0 151	4 054

* Expressed in grams of salt per 100 cc. of solution at 25°. Carter, *Ind. Eng. Ch.*, **20**, 1195 (1928).

Fluorine and fluorides are usually detected[3] by mixing with H_2SO_4 (if necessary) and warming, whereupon the HF liberated will etch a glass surface exposed to it.[4] Silica interferes, but this difficulty may be turned to an advantage by using the "hanging drop" test which depends upon the fact that SiF_4 reacts with H_2O to give a precipitate of silicic acid: 3 SiF_4 + 3 H_2O = H_2SiO_3 + 2 H_2SiF_6. The sample is treated as for the "etch" test except that silica is also added and the glass surface placed over the mixture carries a drop of water. It will become turbid if SiF_4 is liberated. This method is especially satisfactory for the detection of fluorine in silicates. Boron interferes in this as well as in the "etch" test. If a fluoride is treated with HCl then with a zirconium lake of alizarin[5] the red color of the latter will turn yellow almost immediately. Chlorine bleaches the color. Upon heating, in the colorless flame of a Bunsen burner, a mixture of borax, $KHSO_4$ and a fluoride, fused to a bead on a loop of platinum wire, an evanescent yellow-green color is imparted to the flame. Precipitation tests for F^- employing Ca^{++} or Sr^{++} are not as satisfactory as the solubility figures for their salts would indicate because of the colloidal nature of the precipitates; lanthanum acetate is said to be a better reagent.[6] This same compound may be used for the determination of fluorine.[7] One of the standard, although somewhat unsatisfactory, methods is to

[1] Ephraim and Barteczko, *Z. anorg. allgem. Ch.*, **61**, 258 (1909), *C.A.* **3**, 1123, give a classified list of double fluorides. Cf. Gmelin, 8th ed., No. 5, p. 59 *et seq.*

[2] Carter, *Ind. Eng. Ch.*, **22**, 886 (1930), gives available data on the solubility of fluosilicates.

[3] Cf. Gautier and Clausmann, *Compt. rend.*, **154**, 1670 (1912); **158**, 1389, 1631 (1914); **162**, 105 (1916).

[4] Cf. Partridge, *Analyst*, **44**, 234 (1919); Woodman and Talbot, *J. Am. Ch. Soc.*, **28**, 1437 (1906).

[5] Alizarin (0.5 g.) in 200 cc. of alcohol mixed with 1.5 g. of $ZrCl_2$ in 75 cc. of alcohol, filtered, washed with alcohol and suspended in the same medium. Stone, *J. Ch. Education*, **8**, 347 (1931). Cf. Alimarin, *Z. anal. Ch.*, **81**, 8 (1930), *C.A.* **24**, 4479; de Boer, *Rec. trav. ch.*, **44**, 1071 (1925).

[6] Treadwell and Köhl, *Helv. Ch. Acta*, **9**, 470 (1926), *C.A.* **20**, 2801.

[7] Meyer and Schulz, *Z. angew. Ch.*, **38**, 203 (1925). For a critical discussion of the various methods that have been suggested for the determination of fluorine, see: *Anon.*, *Ch. Ztg.*, **45**, 792 (1921), *C.A.* **15**, 3955.

precipitate F^- as CaF_2, which is dried and weighed as such.[1] Another much used procedure is that advocated by Steiger[2] in which the bleaching effect of fluoride on pertitanic acid is measured colorimetrically. Fluorides may also be determined by heating with SiO_2 and H_2SO_4. The SiF_4 volatilized is collected in H_2O and the H_2SiF_6 titrated with standard NaOH[3] or converted to K_2SiF_6 which is titrated with NaOH using phenolphthalein as an indicator.[4] Fluorides may be determined volumetrically by titration with Fe^{+3} using CNS^- as an indicator. The method is unsatisfactory for less than 20 mg. F^-, unless the endpoint is determined electrometically.[5] The lead chlorofluoride method in which the fluorine is precipitated as PbClF and weighed as such or titrated by the Volhard procedure, is considered very satisfactory.[6]

§235. Silicon (and Silicic Acid). (L. *silex* = flint.) Si = 28.06. Atomic No. 14. Valence 4. First prepared by Berzelius in 1823.

Silicon has been described as existing in two modifications, both having the same x-ray pattern, however. *Amorphous* silicon is a dark brown powder prepared by reduction of $SiCl_4$ with Na° at a high temperature ($SiCl_4 + 4\ Na° = Si° + 4\ NaCl$). *Crystalline* or semimetallic silicon is a gray, almost silvery solid obtained by reducing Na_2SiF_6 or SiO_2 with an excess of Al° or by heating SiO_2 with carbon in an electric furnace.[7] It has a density of 2.4; melting point, 1420°; boiling point, 2600°. Silicon is never found free in nature, but always in the combined state as silica, SiO_2, or as a silicate (see below). Calculated as the element it comprises about 28% of the earth's crust and is therefore second only to oxygen in abundance.

Silicon will burn in oxygen, but a surface layer of SiO_2 is quickly formed that tends to hinder further action. It ignites spontaneously in fluorine, unites with Cl[8] above 300°, and with Br at about 500°; action with iodine is slow. As carbon forms series of hydrocarbons so silicon forms at least one series,[9] the silane, corresponding to the methane group in carbon chemistry. The first half-dozen members of the Si_nH_{2n+2} compounds have been prepared. They are all spontaneously inflammable and decomposed by H_2O with formation of SiO_2. The action of the first member, SiH_4, on $AgNO_3$ is somewhat similar to that of AsH_3: $SiH_4 + 4\ AgNO_3 = 4\ Ag + Si° + 4\ HNO_3$. Silicon is insoluble in acids except HF[10] with which it reacts to form the gas SiF_4, non-corrosive and readily hydrolyzed: $3\ SiF_4 + 3\ H_2O = 2\ H_2SiF_6$[11] $+ H_2SiO_3$. Silicon unites with N and with S at high temperatures. Many metals form silicides of the general compositions, M_3Si, M_2Si, MSi_2, etc., e.g., Li_3Si, Mg_2Si, $CaSi_2$. The last named compound is commercially an electric furnace product, obtained by fusing lime, sand and carbon:

[1] Berzelius, *J. Chemie u. Physik*, **16**, 426 (1816).

[2] Steiger, *J. Am. Ch. Soc.*, **30**, 219 (1908).

[3] Reynolds, *et al.*, *J. Assoc. Official Agr. Ch.*, **11**, 225 (1928).

[4] Bayle and Amy, *Compt. rend.*, **188**, 792 (1929), *C.A.* **23**, 2390. Cf. Hönig, *Ch. Ztg.*, **31**, 1207 (1907), *C.A.* **2**, 966.

[5] Treadwell and Köhl, *Helv. Ch. Acta*, **8**, 500 (1925), *C.A.* **20**, 159.

[6] Starck, *Z. anorg. allgem. Ch.*, **70**, 173 (1911), *C.A.* **5**, 2049; Hawley, *Ind. Eng. Ch.*, **18**, 573 (1926).

[7] For the preparation of pure Si°, see: Hölbling, *Z. angew. Ch.*, **40**, 655 (1927).

[8] Usually $SiCl_4$ is obtained by the reaction: $SiO_2 + 2\ C + 2\ Cl_2 = SiCl_4 + 2\ CO$. Higher members, as Si_2Cl_6, etc., are also formed in small amounts.

[9] See especially, Stock, *et al.*, *Ber.*, **49**, 108, 111 (1916); **50**, 1739, 1754, 1764 (1917); **51**, 989 (1918); **56**, 986, 1087, 1695 (1923).

[10] The solubility of Si° in a solution of HF varies with the concentration of that acid. Bedel, *Compt. rend.*, **188**, 1255, 1294 (1929), *C.A.* **23**, 4124.

[11] For the preparation and properties of H_2SiF_6, see: Katz, *Ch. Ztg.*, **28**, 356, 386 (1904); Wagner and Ross, *Ind. Eng. Ch.*, **9**, 1116 (1917).

$CaO + SiO_2 + 5\ C = CaSi_2 + 5\ CO$. It is a powerful reducing agent and is used in the manufacture of steel as a deoxidizer. Ferrosilicon, FeSi, obtained by the reduction of iron ores high in Si, is used to make acid-resisting steel ("duriron" containing 16% Si) and an alloy of high magnetic permeability. Silicon carbide or "carborundum," SiC, is one of the hardest substances known. It also is made in the electric furnace. ($SiO_2 + 3\ C = SiC + 2\ CO$) and is used principally as an abrasive.

Silicon forms two oxides: silicon monoxide, SiO,[1] and silicon dioxide, SiO_2. The former is obtained by heating SiO_2 to 2000° in the presence of a small amount of carbon: $SiO_2 + C = SiO + CO$, and is used as a paint pigment.

Silica, silicic anhydride, SiO_2, is a white, stable solid. It exists in three forms: *quartz*[2] (density 2.65, slightly harder than glass), *tridymite* and *cristobalite*. These may be converted one into another by the application or removal of heat. Silica is found in nature as sand, quartz,[3] opal, flint, etc., or in combination with bases as silicates, as asbestos, soapstone, igneous rocks, etc. All geological formations except chalk contain silicon as the dioxide or a silicate. Silica is used chiefly in the building industry, in the form of sand, as an ingredient of Portland cement [largely Ca_2SiO_4, Ca_3SiO_5 and $Ca_3(AlO_3)_2$], glass ($2\ Na_2CO_3 + CaCO_3 + 6\ SiO_2 \rightarrow Na_2CaSi_6O_{15}$), sodium silicate ("water glass"), etc.

Pure amorphous silica may be prepared by fusing finely powdered quartz with Na_2CO_3, dissolving the cooled mass in water, and pouring into fairly concentrated HCl. The precipitate is filtered, well washed and ignited. Another method involves the hydrolysis of SiF_4 followed by washing and ignition of the gelatinous precipitate.

Silica is insoluble[4] in water or acids except HF, which dissolves it with formation of gaseous silicon fluoride, SiF_4. Among the silicates only those of the fixed alkalis[5] are soluble in water. These silicates, in solution, are readily decomposed by acids, including carbonic, forming gelatinous silicic acid. While anhydrous SiO_2 is insoluble in mineral acids, the freshly precipitated hydrate is soluble (see below) in those acids. Silicic acid is decomposed by evaporation to dryness in the presence of mineral acids, with separation of the anhydrous SiO_2, which is insoluble in more of the same acid that previously had effected its solution. From another standpoint the "solution" of silicates in acids may be merely a case of their peptization by hydrogen ions. Although silica is said to form at least two hydrates, orthosilicic acid, H_4SiO_4, and metasilicic acid, H_2SiO_3, it is believed by some investigators that definite compounds corresponding to the formulas given do not exist, and that $xSiO_2 \cdot 2yH_2O$ and $xSiO_2 \cdot yH_2O$, where x and y are approximately of the same value, more closely fit the facts.[6] While many of the salts of these acids are admittedly very complex, resembling in this respect derivatives of boric, tungstic and molybdic acids, a number of the metal monosilicates may be divided into groups corresponding fairly closely to the ortho type, e.g., zircon, $ZrSiO_4$, and the meta type, e.g., wollastonite, $CaSiO_3$. In addition there are basic ortho- and metasilicates and, among the simpler of the complicated compounds, derivatives of disilicic acid, $H_2Si_2O_5$, and trisilicic acid, $H_4Si_3O_8$, e.g., the feldspars as $(K, Na)AlSi_3O_8$.[7]

Solutions of the alkali silicates precipitate ions of all other metals through formation

[1] Potter, *Electroch. Met. Eng.*, **5**, 442 (1907).

[2] Cf. Smits and Endell, *Z. anorg. allgem. Ch.*, **80**, 176 (1913), *C.A.* **7**, 2729. For the chemical behavior of quartz, tridymite, etc., see: Schwarz, *Ibid.*, **76**, 422 (1912), *C.A.* **6**, 3238.

[3] Quartz crystals are usually very pure SiO_2. Some deposits of sand have been found that contain over 99.9% SiO_2, but they are not plentiful.

[4] Lenher and Merrill, *J. Am. Ch. Soc.*, **39**, 2630 (1917), have determined the solubility of SiO_2 in H_2O, HCl and H_2SO_4 at 90°. Within limits, the solubility is decreased by an increase in acidity.

[5] Commercial sodium silicate, "water glass," is made by fusing sand, Na_2CO_3 and carbon and extracting the glassy melt in an autoclave, or by dissolving SiO_2 in NaOH.

[6] Cf. Dilthey and Nagel, *J. prakt. Ch.*, **129**, 178 (1931), *C.A.* **25**, 2068; Thiessen and Koerner, *Z. anorg. allgem. Ch.*, **182**, 343 (1929), *C.A.* **23**, 5427; Schwarz and Menner, *Ber.*, **58**, 73 (1925), *C.A.* **19**, 941; Lenher, *J. Am. Ch. Soc.*, **43**, 391 (1921).

[7] Cf. Latimer and Hillebrand, pp. 238–41.

of insoluble silicates.[1] These salts are decomposed by acids with the separation of gelatinous silicic acid. Evaporation dehydrates silicic acid, leaving a residue of silica, SiO_2. Ammonium salts precipitate silicic acid from solutions of potassium or sodium silicate: $Na_2SiO_3 + (NH_4)_2CO_3 = Na_2CO_3 + 2\ NH_3 + H_2SiO_3$. In the process of analysis any silicic acid not removed in the first group by HCl, will be precipitated in Group III on the addition of NH_4Cl.

Silicates fused with the alkalis form soluble alkali silicates, and oxides of the metal displaced. If alkali carbonates are employed the same products are formed with evolution of CO_2. Silica, SiO_2, is also changed to a soluble silicate by fusion with fixed alkali hydroxides or carbonates. It does not react with Na_2SO_4 until a temperature of over 1100° is reached. In a fused bead of microcosmic salt particles of silica swim undissolved. If a silicate is used, its base will dissolve in most cases leaving a "skeleton of silica" in the liquid bead. With a bead of Na_2CO_3, silica and most of the silicates fuse to a clear glass.

Silicic acid may be detected by a method based upon the formation of a stable heteropoly-acid, $SiO_2 \cdot 12MoO_3 \cdot xH_2O$, yellow in color. The unknown is treated with a neutral solution of ammonium molybdate, the mixture slightly acidified and then a few drops of $SnCl_2$ added, whereupon a deep blue color develops if more than one part in a million of silicic acid is present.[2] Another test applicable to silicic acid, silica or a silicate involves the treatment of a sample with HF.[3] Some of the SiF_4 evolved is absorbed in a drop of H_2O suspended over the reaction mixture. Due to hydrolysis a precipitate of silicic acid forms in the drop: $3\ SiF_4 + 3\ H_2O = H_2SiO_3 + 2\ H_2SiF_6$.[4]

The most important method for the determination of Si in silica or a silicate is to fuse a finely powdered sample in a platinum crucible with about six times its weight of Na_2CO_3. The cooled melt is transferred to a beaker, covered with water, then decomposed with an excess of HCl. Evaporation to dryness and baking converts most of the silicic acid to insoluble SiO_2 which is removed by filtration after dissolving the soluble salts in HCl. The filtrate is again evaporated to dryness, baked, and the remaining silica removed as described. The precipitate is washed, dried, ignited and weighed. It is then treated with HF and H_2SO_4 which convert the SiO_2 into volatile SiF_4. The residue is again ignited and weighed. The loss in weight represents the amount of silica in the original sample.[5]

§236. Phosphorus (Gr. *phosphorus* = light bringer). P = 31.02. Atomic No. 15. Valence 3 and 5. First prepared by Brandt in 1669.

1. Physical Properties. — Phosphorus exists in several allotropic modifications. Ordinary "white" phosphorus is colorless and of a waxy appearance. Its density is 1.82; melting point, 44.3°; boiling point, 280°; the molecular weight corresponds to P_4 (above 1500° to P_2). Ordinary yellow phosphorus, when freshly prepared, is a transparent solid but becomes coated with a thin white film when placed in water containing air. Heated above the boiling point in the absence of air it sublimes as a colorless gas, depositing lustrous transparent crystals. At low temperatures phosphorus oxidizes slowly in the air with a characteristic odor, due in part to the ozone formed. It ignites spontaneously in the air at 60°, to burn with a bright yellow light and much heat. In a finely divided state (as obtained from the evaporation of a CS_2 solution) it ignites spontaneously at temperatures at which the compact phosphorus may be kept for days. It must be kept under water. Great caution should be exercised when working with yellow phosphorus. Burns caused by it are very painful and heal with great diffi-

[1] For preparation of the metal silicates, see: Jordis, *et al.*, (*C.A.* **2**, 2050).

[2] Oberhauser and Schormüller, *Z. anorg. allgem. Ch.*, **178**, 381 (1929), *C.A.* **23**, 2906.

[3] The sample may be mixed with CaF_2 and concentrated H_2SO_4, then warmed.

[4] For other methods, see: Gutzeit, *Helv. Ch. Acta*, **12**, 713 (1929), *C.A.* **23**, 4645.

[5] Lenher and Truog, *J. Am. Ch. Soc.*, **38**, 1050 (1916), have made a careful study of the determination of silica. Cf. Hillebrand and Lundell, p. 540, 720.

culty. Taken internally it is very poisonous, 0.1 g. normally being a fatal dose. If the vapors are breathed for any length of time necrosis of the jaw will develop ("phossy jaw"). Ordinary phosphorus is luminous in the dark, but it has been shown that at least small amounts of oxygen are necessary. The presence of H_2S, SO_2, CS_2, Br, Cl, etc., prevents the glowing. Upon heating in the absence of air, e.g., in sealed tubes, to 250°, it changes to the red modification.

Red phosphorus is a dull red, tasteless powder. It apparently does not have a definite density or melting point but is a mixture of the white and purple forms. It is only slightly poisonous, is not particularly reactive and needs no special precautions for its preservation (distinction from the white variety). It does not melt when heated to redness in the absence of air but sublimes to give the crystalline form, the change commencing at 260°. Heated in air, at about 260° it ignites. Two other varieties of phosphorus are the black and the purple forms. Apparently the latter is the most stable of all. Its density is 2.34; melting point, 590° (at 43 atmospheres). It is obtained by crystallization from solution in molten lead.[1] Phosphorus is chiefly used as "superphosphate," $Ca(H_2PO_4)_2$, to increase soil fertility. This fertilizer is made by treating ground phosphate rock with dilute sulfuric acid: $Ca_3(PO_4)_2 + 2\ H_2SO_4 + 4\ H_2O = Ca(H_2PO_4)_2 + 2\ CaSO_4{\cdot}2H_2O$ (gypsum). Practically all of the P° manufactured is used for making matches in which it is ordinarily present as P_4S_3. A small amount of white phosphorus mixed with grease, flour, etc., is used as a rat poison.

2. Occurrence. — Phosphorus is never found free in nature. Plants extract it from the soil, and animals get it from the plants. Hence traces are found in nearly all animal and vegetable tissues, particularly in the seeds of plants and the bones of animals. Phosphorus occurs principally as "phosphate rock," an impure variety of apatite, $Ca_5F(PO_4)_3$, analyzing 15%–40% P_2O_5. Its color varies from white through gray and brown to black. It is found widely scattered over the world. In 1929 the countries of northern Africa — Tunisia, Algeria, Morocco and Egypt — produced about 50% of the world's supply, while the United States — Florida, South Carolina, Tennessee, Idaho, Utah and the neighboring states — contributed slightly over 36%. The total amount of rock mined that year was about 10.5 million metric tons.[2] While the price of phosphate rock depends on the phosphorus content and other factors, in the United States it may vary from $3 to $5 per ton at the mine. The white form of the element sells for about 35 cents per pound, the red form is almost twice as expensive.

3. Preparation. — As indicated above, practically all of the phosphorus sold commercially is in the form of superphosphate, $Ca(H_2PO_4)_2$, obtained by digesting ground rock phosphate with H_2SO_4. Free phosphorus may be prepared by heating calcium phosphate with sand and carbon and condensing the vapor under water: $Ca_3(PO_4)_2 + 3\ SiO_2 + 5\ C = P_2 + 3\ CaSiO_3 + 5\ CO$. Red or amorphous phosphorus is secured by heating white phosphorus for about forty hours at 240° to 250° in the absence of air or under pressure at 300° for a few minutes. It is washed with CS_2 to remove traces of white phosphorus, then dried at 100°.

4. Hydrides, Oxides and Acids. — *Phosphine*, PH_3, is a colorless, poisonous, odoriferous gas. If solidified it melts at − 132.5° and boils at − 86.2°. When pure it ignites only upon heating to about 100°. As ordinarily prepared, however, it contains some P_2H_4, which promotes spontaneous combustion on exposure to the air: $PH_3 + 2\ O_2 = H_3PO_4$. Phosphine may be made (*a*) by treating aluminum phosphide with dilute H_2SO_4,[3] or calcium phosphide with H_2O: $Ca_3P_2 + 6\ H_2O = 2\ PH_3 + 3\ Ca(OH)_2$; (*b*) by dissolving white phosphorus in an alkali hydroxide: $P_4 + 3\ NaOH +$

[1] For further data concerning the allotropic forms of P°, see: Smits, *Compt. rend.*, **188**, 390 (1929), *C.A.* **23**, 2614; Nikolaev, *J. Russ. Phys. Ch. Soc.*, **60**, 1045 (1928), *C.A.* **23**, 2332; Bridgeman, *J. Am. Ch. Soc.*, **36**, 1344 (1914).

[2] A metric ton is 1000 kg. or 2205 lbs.

[3] Moser and Brukl, *Z. anorg. allgem. Ch.*, **121**, 73 (1921), *C.A.* **16**, 2822.

$3H_2O = PH_3 + 3\ NaH_2PO_2$. Phosphine reacts with some metal ions to produce phosphides, most of which are of uncertain composition (Cu^{++} and Hg^{++} are said to form Cu_2P and Hg_3P_4). It also reacts to form some compounds: $PH_3 + HI = PH_4I$. The bromide may be prepared in the same way but the chloride is obtained only under high pressure.[1]

Phosphine may be detected by (*a*) its odor, (*b*) its reaction with a test paper[2] impregnated with 10% $CuSO_4$, or $HgCl_2$, or 0.1 *N* $AgNO_3$. The last mentioned reagent will reveal a concentration of PH_3 of 10^{-6}. The approximate determination of PH_3 may be effected by passing the gas into a solution of $HgCl_2$, filtering off the yellow precipitate and titrating the filtrate with 0.1 *N* NaOH, using methyl orange as an indicator. The composition of the precipitate is variable but three molecules of HCl are always liberated per molecule of phosphine: $PH_3 + 3\ HgCl_2 = P(HgCl)_3 + 3\ HCl$.[3]

Phosphorus forms at least three *oxides*, P_2O_3, P_2O_4 and P_2O_5, of which the last mentioned is probably the most important. *Phosphorus trioxide*, P_2O_3, is a snow-white solid obtained by burning P° in a limited amount of air. It melts at 22.5° and boils at 173.1°.[4] The vapor density of the gaseous oxide indicates the molecular formula P_4O_6. It has an odor resembling that of P°. Heated in a sealed tube at 200° it decomposes into P_2O_4 and P°. Upon exposure to air it oxidizes to P_2O_5. It is readily separated from P_2O_5 by taking advantage of its greater volatility. It is slowly soluble in cold water to form phosphorous acid; in hot water the action is more complex: $2\ P_2O_3 + 6\ H_2O = PH_3 + 3\ H_3PO_4$. *Phosphorus pentoxide,* P_2O_5, is easily made by burning P° in an excess of air.[5] In the anhydrous condition it is snow white and a very efficient drying agent. It will even remove H_2O from concentrated H_2SO_4. On contact with H_2O it dissolves with a hissing sound to form phosphoric acid, H_3PO_4.[6]

Among the *acids* of phosphorus, reported in the literature, the following have been fairly well established:

hypophosphorous	H_3PO_2	orthophosphoric[8]	H_3PO_4
orthophosphorous[7]	H_3PO_3	pyrophosphoric	$H_4P_2O_7$
pyrophosphorous	$H_4P_2O_5$	metaphosphoric	HPO_3
hypophosphoric	$H_4P_2O_6$ (or H_2PO_3)	peroxymonophosphoric	H_3PO_5
		peroxydiphosphoric	$H_4P_2O_8$

[1] For other reactions of PH_3, see: Moser and Brukl, *loc. cit.*
[2] Wilmet, *Compt. rend.*, **184**, 1456 (1927), *C.A.* **21**, 3030.
[3] Wilmet, *Ibid.*, **185**, 206 (1927), *C.A.* **21**, 3175.
[4] Thorpe and Tutton, *J. Ch. Soc.*, **57**, 545 (1890).
[5] Cf. Finch and Peto, *J. Ch. Soc.*, **121**, 692 (1922); Manley, *Ibid.*, p. 331.
[6] Balareff, *Z. anorg. allgem. Ch.*, **69**, 215 (1910), *C.A.* **5**, 1032.
[7] Usually the prefix ortho is omitted.
[8] Ortho-, pyro- and metaphosphoric acids will be discussed in §237, p. 492.

Hypophosphorous acid, H_3PO_2, is a colorless, syrupy liquid, melting point, 26.5°; density, 1.493 at about 19°. Although containing three hydrogen atoms it is monobasic[1] and forms but one series of salts, e.g., NaH_2PO_2, $Ba(H_2PO_2)_2$, etc.; it is, however, a stronger acid than H_3PO_4. The acid is prepared by warming P° with $Ba(OH)_2$ until PH_3 ceases to be evolved. Any excess Ba^{++} is removed by precipitation with CO_2. The filtrate is evaporated to crystallization of the barium salt. This is dissolved in H_2O and decomposed by addition of the calculated amount of H_2SO_4. The filtrate may be concentrated and the solid H_3PO_2 isolated by evaporating off the H_2O below 110° (H_3PO_2 + heat → PH_3 + H_3PO_4). The free acid is readily miscible with water in all proportions. The salts are all soluble in H_2O and a number of them will dissolve in alcohol.

Hypophosphorous acid is a very powerful reducing agent, being readily oxidized to a phosphate: Pb^{+4} becomes Pb^{++}, Ag^{+}[2] forms Ag°, Hg^{++} gives first Hg_2^{++} then Hg° in either acid or alkaline solution; arsenates and arsenites are reduced to As° in HCl solution; Bi^{+3} becomes Bi° in the presence of alkalis or acetic acid; Cu^{++} on boiling forms Cu° (separation from Cd); Fe^{+3}, Cr^{+6}, Co^{+3}, Ni^{+4} and $Mn^{>+2}$ are reduced in acid solution to Fe^{++}, Cr^{+3}, Co^{+2}, Ni^{+2} and Mn^{+2} respectively. They are not affected in alkaline solution.

Among the non-metals, HNO_3 and HNO_2 become NO; H_2SO_3 forms S° and some H_2S; H_2SO_4 becomes H_2SO_3 which is further reduced as just indicated; Cl°, ClO^- and ClO_3^- are all reduced to Cl^- in acid or alkaline mixture; the same is true of the corresponding Br and I[3] ions.

Hypophosphorous acid may be distinguished from phosphorous acid by adding $CuSO_4$ to the free acid and warming to 55°. With H_3PO_2 a dark red precipitate is first formed which, upon raising the temperature to 100°, is decomposed with the deposition of Cu° and the evolution of H_2; with H_3PO_3 no intermediate compound is obtained. Hypophosphorous acid reduces MnO_4^- immediately, phosphorous acid only after some time. Phosphites precipitate Ba^{++}, Sr^{++} and Ca^{++}, while hypophosphites do not. When H_3PO_2 is treated with Zn° and H_2SO_4 it is converted to PH_3. On boiling H_3PO_2 with excess of an alkali hydroxide, first a phosphite then a phosphate is formed with evolution of hydrogen.

Hypophosphorous acid may be determined (*a*) by oxidation with HNO_3 to PO_4^{-3} followed by precipitation and weighing as the phosphomolybdate or $Mg_2P_2O_7$; (*b*) by heating with $HgCl_2$ below 60°, the precipitate of Hg_2Cl_2

[1] Cf. Mitchell, *J. Ch. Soc.*, **117**, 957 (1920), *C.A.* **14**, 3353.

[2] Cf. Sieverts and Loessner, *Z. anorg. allgem. Ch.*, **76**, 1 (1912), *C.A.* **6**, 2719; Sieverts, *Ibid.*, **64**, 29 (1909), *C.A.* **4**, 1277, for the action of H_3PO_2 on various metallic salts.

[3] Cf. Hovorka (*C.A.* **25**, 1452). Mitchell has published a number of articles on the action of H_3PO_2, e.g., *J. Ch. Soc.*, **117**, 1322 (1920); **119**, 1266 (1921); **121**, 1624 (1922); **125**, 564 (1924).

being dried and weighed as such: $NaH_2PO_2 + 4\ HgCl_2 + 2\ H_2O = 2\ Hg_2Cl_2 + H_3PO_4 + NaCl + 3\ HCl$.

Orthophosphorous acid, H_3PO_3, is a crystalline solid, very deliquescent, melting at 73.6°, density 1.651 at 21.2°. It is a dibasic acid[1] forming salts of the types NaH_2PO_3 and Na_2HPO_3. This compound is made by dissolving P_2O_3 in an excess of water or by the hydrolysis of PCl_3: $PCl_3 + 3\ H_2O = H_3PO_3 + 3\ HCl$. The acid itself is miscible with H_2O in all proportions. The alkali phosphites are soluble in H_2O; most of the others are insoluble (distinction from hypophosphites). As an acid H_3PO_3 is stronger than H_3PO_4. It is also a strong reducing agent, changing to H_3PO_4 even on exposure to the air. It reduces Ag^+, Au^+ and Au^{+3} to the metallic state and is changed to a phosphate by most of the strong oxidizing acids and by many of the higher metallic oxides. Hg^{++} and Cu^{++} are reduced to the lower valence and then to the metal. Concentrated H_2SO_4, with heat, forms H_3PO_4 and SO_2. Nascent hydrogen ($Zn^\circ + H_2SO_4$) produces PH_3. With iodine two essentially different reactions occur, one predominating in a solution of high acidity, the other in low concentration of H^+.[2] The acid is decomposed upon ignition; the same is true of its salts.

Orthophosphorous acid may be detected indirectly by oxidation to H_3PO_4 which is readily identified (§237). It is distinguished from H_3PO_2 as indicated above, also by the difference in solubility of the salts of the two acids. It is determined by oxidation to H_3PO_4, which is measured as described below.

Apparently *metaphosphorous acid* has not been isolated. *Pyrophosphorous acid*, $H_4P_2O_5$, is obtained by the interaction of PCl_3 and water: $2\ PCl_3 + 5\ H_2O = H_4P_2O_5 + 6\ HCl$. It melts at 38° and decomposes at 130°. A number of pyrophosphites have been prepared but they are of minor importance here.[3]

Hypophosphoric acid, $H_4P_2O_6$[4] (or H_2PO_3), is one of the products of the slow oxidation of P° in moist air. It is also obtained by oxidizing P° with $KMnO_4$ in strong alkaline solution.[5] The acid consists of small, colorless, hygroscopic crystals melting at 55°, decomposing at about 70° into H_3PO_3 and HPO_3. It is oxidized to H_3PO_4 by warm HNO_3, slowly by $KMnO_4$ in the cold, rapidly when heated. It is not oxidized by H_2O_2, dilute hypochlorite or H_2CrO_4. It is not reduced by Zn° and H_2SO_4 (distinction from H_3PO_2 and H_3PO_3). A solution of Ag^+ gives a white precipitate that does not blacken in the light (distinction from H_3PO_2 and H_3PO_3). It forms

[1] Cf. Palazzo and Maggiacomo, *Gazz. ch. ital.*, **38**, II, 115 (1908), *C.A.* **2**, 3038.

[2] Steele, *J. Ch. Soc.* (*Proc.*), **24**, 193 (1908). Cf. Mitchell, *J. Ch. Soc.*, **123**, 2241 (1923).

[3] Amat, *Compt. rend.*, **106**, 1400 (1888); **108**, 1056 (1889); **110**, 1191 and 901 (1890).

[4] Rosenheim and Zilg, *Z. physik. Ch.*, *Abt. A*, **139**, 12 (1928), *C.A.* **23**, 1584.

[5] Vogel, *Z. angew. Ch.*, **42**, 263 (1929), *C.A.* **23**, 2383. Cf. Cavalier and Cornec, *Bull. soc. ch.*, [4] **5**, 1058 (1909), *C.A.* **4**, 725; Rosenheim and Pinsker, *Ber.*, **43**, 2003 (1910), *C.A.* **4**, 2778.

four series of salts, all four hydrogen atoms being replaceable by a metal.[1] The hypophosphates are much more stable toward oxidizing agents than hypophosphites or phosphites.

The *peroxyphosphoric acids*,[2] H_3PO_5 and $H_4P_2O_8$ are formed by the electrolysis of a solution of HPO_4^{--} containing a little F^- and $Cr_2O_7^{--}$; a high current density gives H_3PO_5, while a lower amperage favors the production of $H_4P_2O_8$. The former acid may also be prepared by treating P_2O_5 with cold perhydrol (30% H_2O_2).[3]

5. Solubilities. — A trace of phosphorus dissolves in H_2O (1 : 300,000). Alcohol dissolves 0.4%, ether 0.9%, olive oil 1%, turpentine 2.5%, while carbon disulfide will take up 10 to 15 times its own weight. Red phosphorus is insoluble in these solvents. Yellow phosphorus is soluble in hot alkalis with evolution of PH_3; red phosphorus is not affected.

6. Reactions. — When phosphorus is boiled with a fixed alkali or alkaline earth hydroxide, phosphine, PH_3, hypophosphite, $H_2PO_2^-$, and some phosphate, PO_4^{-3}, are formed. When warmed in an atmosphere of N or CO_2 phosphorus combines directly with many metals to form phosphides: Hg_3P_4, MnP_2, Sn_3P, K_2P_5, PbP_5, etc.; some metal oxides (Ca) and salts[4] (Ag, Cu) react similarly. These phosphides are usually brittle solids, decomposing in water or dilute acids to form PH_3. In nearly all of the reactions of phosphorus both the white and red varieties react the same, the latter with much less intensity, and frequently requiring the aid of heat. When mixed with PbO_2, Pb_3O_4, HgO, Ag_2O, $K_2Cr_2O_7$, and when heated with CuO or MnO_2, phosphorus is ignited. Solutions of Pt, Au, Ag and Cu salts ultimately yield a precipitate of the corresponding metal.

Phosphorus in all of its valences lower than five is readily oxidized to PO_4^{-3} by HNO_3 or aqua regia. Any moderately strong oxidizing agent will effect the same result.[5] Phosphorus combines with O_2 to form oxides (see p. 488). With yellow phosphorus the reaction begins at room temperature, with the red variety at about 260°. Sulfur and red phosphorus interact at ordinary temperatures, forming P_4S_3 (used for making matches), P_2S_3, P_2S_5 (used in organic chemistry) and PS_6, the product depending upon the ratio of the elements employed. Yellow phosphorus and S° unite explosively. Chlorine or bromine reacts vigorously with P° at room temperature, forming, e.g., PCl_2, PCl_3 or PCl_5, depending upon the amount of halogen used. Iodine forms only PI_3. These phosphorus halides are de-

[1] Cf. Müller, *Z. anorg. allgem. Ch.*, **96**, 29 (1916), *C.A.* **11**, 1379, concerning the basicity of this acid.

[2] The phosphoric acids should logically be discussed here but they are of sufficient importance to occupy a separate section, §237.

[3] Fuhrmann, *Ch. Ztg.*, **45**, 437 (1921), *C.A.* **15**, 2397; Schmidlin and Massini, *Ber.*, **43**, 1162 (1910), *C.A.* **4**, 1947.

[4] Walker, *J. Ch. Soc.*, **1926**, 1370.

[5] Rosenstein, *J. Am. Ch. Soc.*, **42**, 883 (1920), has suggested the use of red phosphorus as a reducing agent for qualitative analysis.

composed by H_2O with formation of the corresponding hydracid and a variety of phosphorus acids depending upon conditions (see above). In the presence of H_2O phosphorus may be oxidized to H_3PO_4 by Cl, Br, I, ClO_3^-, BrO_3^-, or IO_3^-: $P_4 + 10\ Cl_2 + 16\ H_2O = 4\ H_3PO_4 + 20\ HCl$.

8. Detection. — Phosphorus may be detected (*a*) by its phosphorescence, (*b*) by conversion to PH_3 when boiled with NaOH or treated with Zn° and H_2SO_4,[1] the PH_3 being identified with $AgNO_3$ or $HgCl_2$ test paper (cf. phosphine above). Another way to use the $AgNO_3$ paper is to hang it in a closed flask above the sample to be tested then place the flask in warm water (30° to 40°). The paper will soon turn black if even a small amount of yellow phosphorus is present, the Ag^+ being reduced to Ag° by the vapor.

9. Determination. — Phosphorus may be determined by oxidation to phosphate which is treated as described below.[2]

§237. Phosphoric Acids. H_3PO_4, $H_4P_2O_7$, HPO_3

1. Physical Properties. — Phosphoric anhydride, P_2O_5, dissolves in water to form three varieties of phosphoric acid: *ortho*, H_3PO_4; *pyro*, $H_4P_2O_7$;[3] and *meta*, HPO_3. Orthophosphoric acid is a translucent, crystallizable and very deliquescent solid; its density is 1.88, melting point, 42.3°.[4] Upon heating, it is changed first to pyrophosphoric acid, then to metaphosphoric acid. Orthophosphoric acid forms three classes of salts: primary, monobasic or monometallic phosphates — $M^+H_2PO_4$; secondary, dibasic or dimetallic phosphates — $M_2^+HPO_4$; and tertiary, tribasic, trimetallic or normal orthophosphates — $M_3^+PO_4$. Primary sodium phosphate, NaH_2PO_4, 0.2 *M* has a pH = 5 +, i.e., is neutral to methyl orange, slightly acid to litmus and distinctly acid to phenolphthalein. Secondary sodium phosphate, Na_2HPO_4, 0.2 *M* has a pH = 8, i.e., is distinctly alkaline to methyl orange, slightly alkaline to litmus and neutral to phenolphthalein. In other words, one H of H_3PO_4 may be titrated with NaOH, using methyl orange as an indicator, two H's may be titrated using phenolphthalein.[5]

Pyrophosphoric acid[6] is a soft, glass-like solid or opaque crystalline mass. The crystals separate from the syrupy solution at −10°. They melt at 61° and are very

[1] This method is obviously an application of the Gutzeit test for arsenic. Cf. Ericsson (*C.A.* **8**, 35); Leclere, *J. pharm. ch.*, [7] **5**, 15 (1912), *C.A.* **6**, 1893.

[2] For methods of separation and determination of the phosphorous acids, see: Rosenheim and Pinsker, *Z. anorg. allgem. Ch.*, **64**, 327 (1909), *C.A.* **4**, 553; Van Name and Huff, *Am. J. Sci.*, **45**, 91 (1918); Wolf and Jung, *Z. anorg. allgem. Ch.*, **201**, 337–60 (1931), *C.A.* **26**, 938.

[3] There is considerable evidence for the view that $H_4P_2O_7$ and HPO_3 are polymerized in solution, the former to $(H_4P_2O_7)_{4\text{ or }5}$ and the latter to $(HPO_3)_{2-8}$. The simpler formulas will be used here.

[4] If a solution of H_3PO_4 is evaporated under reduced pressure, $H_3PO_4 \cdot \frac{1}{2}H_2O$ is obtained, which melts at 29.4°.

[5] Concerning the ionization relations of H_3PO_4 and its salts, see: Jowett and Millet, *J. Am. Ch. Soc.*, **51**, 1004 (1929); Kugelmass, *Bioch. J.*, **23**, 587 (1929), *C.A.* **24**, 13; Prideaux, *J. Ch. Soc.*, **99**, 1224 (1911); Abbott and Bray, *J. Am. Ch. Soc.*, **31**, 729 (1909).

[6] Concerning the structure of this acid, see: Balareff, *Z. anorg. allgem. Ch.*, **118**, 123 (1921), *C.A.* **16**, 1194.

soluble in, but unchanged by, water at room temperature. The pyro acid is changed by boiling water to H_3PO_4. Heated to redness, HPO_3 is formed. Pyrophosphoric acid yields two classes of salts: $M_2{}^+H_2P_2O_7$ and $M_4{}^+P_2O_7$.[1] Solutions of its salts may be heated but the presence of a strong acid causes reversion to the ortho form. Metaphosphoric acid is a waxy, white solid, volatile at a red heat. It is a monobasic acid, but there are various polymeric modifications, e.g., $(HPO_3)_2$, $(HPO_3)_3$, $(HPO_3)_6$, etc.,[2] distinguished from each other by physical differences of the acids and by their salts.[3] Metaphosphoric acid is unstable in aqueous solution. At room temperature it reverts to H_3PO_4 in a few days. The course of this reaction is believed by some investigators to involve the intermediate formation of the pyro acid ($HPO_3 \rightarrow H_4P_2O_7 \rightarrow H_3PO_4$), while others insist that the HPO_3 changes directly to H_3PO_4.[4] Both groups are apparently agreed, however, on the point that the reaction is distinctly more complex than is indicated by the equation: $HPO_3 + H_2O = H_3PO_4$.

2. Occurrence. — See: p. 487.

3. Preparation. — *Orthophosphoric acid* may be prepared by dissolving P_2O_5 (§236, 4) in an excess of H_2O. Impure commercial H_3PO_4 is made by heating pulverized phosphate rock with H_2SO_4: $Ca_3(PO_4)_2 + 3\ H_2SO_4 = 2\ H_3PO_4 + 3\ CaSO_4$. Another method involves ignition of the rock mixed with silica and charcoal. The phosphorus evolved is mixed with air to form P_2O_5 which is absorbed in H_2O: $Ca_3(PO_4)_2 + 3\ SiO_2 + 5\ C = 2\ P^\circ + 3\ CaSiO_3 + 5\ CO$; $4\ P^\circ + 5\ O_2 = 2\ P_2O_5$; $P_2O_5 + 3\ H_2O = 2\ H_3PO_4$. When H_3PO_4 is evaporated in a vacuum over H_2SO_4 it is converted to hard, transparent deliquescent crystals that melt at 38.6° and commence to lose H_2O at about 160°. Continued heating[5] to 215° yields *pyrophosphoric acid.* This compound may also be obtained by heating Na_2HPO_4. It first melts in its water of crystallization then, upon removal of the H_2O, solidifies as $Na_4P_2O_7$ which may be converted to $H_4P_2O_7$. The treatment of $Pb_2P_2O_7$ with H_2S[6] and the precipitation of the Ba^{++} by means of H_2SO_4 from a solution of $Ba_2P_2O_7$ are additional methods that have been advocated. Salts of pyrophosphoric acid are formed by double decomposition with $Na_4P_2O_7$; by the action of $H_4P_2O_7$ on certain oxides or hydroxides; or by the ignition of secondary orthophosphates. $Na_2H_2P_2O_7$ may be prepared by titrating a saturated solution of $Na_4P_2O_7$ with HNO_3 until the solution is acid to methyl orange. Upon standing the desired salt separates as large crystals.[7] If H_3PO_4 is heated to dense white fumes a transparent, highly deliquescent, glassy mass is obtained. It is called "glacial" phosphoric acid and is chiefly *metaphosphoric acid,* $(HPO_3)_n$. Further heating for a few hours gives a product that crackles in contact with H_2O but finally dissolves; still longer heating yields an insoluble residue which volatilizes at a bright red heat. The vapor is said to be $(HPO_3)_2$. Metaphosphoric acid may also be obtained by the spontaneous deliquescence of P_2O_5, by adding the calculated amount of H_2O to P_2O_5, by the decomposition of lead metaphosphate with H_2S or of the barium salt with H_2SO_4. *Metaphosphates* are formed by double decomposition with $NaPO_3$ or by fusion of a primary phosphate or any phosphate having but one hydrogen substituted by a metal the oxide of which is non-volatile, e.g., $NaNH_4HPO_4$.

5. Solubilities. — All of the phosphoric acids are readily soluble in water (see above). Alkali primary orthophosphates in solution have an

[1] Cf. Kolthoff, *Pharm. Weekblad,* **57**, 474 (1920), *C.A.* **14**, 3011, concerning the third and fourth dissociation constants of $H_4P_2O_7$.

[2] At least eight have been identified.

[3] Cf. Pascal, *Compt. rend.,* **177**, 1298 (1923), *C.A.* **18**, 505; Holt and Myers, *J. Ch. Soc.,* **99**, 390 (1911); **103**, 532 (1913).

[4] Holt and Myers, *J. Ch. Soc.,* **99**, 384 (1911); Balareff, *Z. anorg. allgem. Ch.,* **68**, 266 (1910), *C.A.* **4**, 2420.

[5] A better way is to heat until a sample, cooled and dissolved in H_2O, gives no yellow precipitate with $AgNO_3$.

[6] Cf. Holt and Myers, *J. Ch. Soc.,* **99**, 384 (1911).

[7] Knorre, *Z. angew. Ch.,* **5**, 639 (1892).

acid reaction, the secondary and tertiary phosphates are alkaline.[1] The latter are easily decomposed, even by CO_2, to form the secondary salt.[2] A number of non-alkali primary orthophosphates are soluble in H_2O, e.g., $Ca(HPO_4)_2$. All normal and secondary orthophosphates are insoluble[3] except those of the alkalis. The normal and secondary phosphates of the alkalis precipitate from solution ions of all other metals. The precipitate is a normal,[4] secondary or basic phosphate, except that with the chlorides of Hg and Sb it is not a phosphate but an oxide or an oxychloride. All phosphates are dissolved or transposed by HNO_3, HCl, or H_2SO_4, and all are dissolved by $HC_2H_3O_2$ except those of Pb, Al and Fe^{+3}. All are soluble in H_3PO_4 except those of Pb, Sn, Hg and Bi.

The non-alkali pyro- and metaphosphates are generally insoluble in water. The pyrophosphates of the alkaline earth metals are difficultly soluble in acetic acid. Many of the pyrophosphates of the heavy metals, except Ag, are soluble in solutions of alkali pyrophosphates, giving solutions that fail to show many of the reactions of the metals involved,[5] e.g., Fe^{+3} as a double pyrophosphate loses the characteristic properties of that ion.

6. Reactions. — *A*. **With metals and their compounds.**[6] — Phosphoric acid dissolves some metals, as Fe, Zn and Mg, with evolution of hydrogen. It reacts with the oxides and hydroxides of the alkalis and alkaline earths and with other freshly precipitated oxides and hydroxides except perhaps Sb_2O_3. It also decomposes all carbonates with evolution of CO_2. Phosphates are formed in the above reactions, the composition of which depends upon conditions. Phosphoric acid is a useful solvent for some substances that resist other reagents. Heated at 230° for about three hours, Si dissolves; carborundum is entirely decomposed in the same time; Zr requires only a few minutes. Upon dilution of the solutions no precipitate is obtained.[7]

A solution of orthophosphoric acid gives no precipitate with ordinary salts of Groups III, IV and V (in the case of Fe^{+3} a distinction from pyro- and metaphosphoric acids) but does form a precipitate with Ag^+ and Pb^{++}. Distinctly ammoniacal solutions of Ca^{++} or Ba^{++} precipitate the

[1] Menzel and Gäbler, *Z. anorg. allgem. Ch.*, **177**, 187 (1928), *C.A.* **23**, 2114, give the solubility of KH_2PO_4 as 25.12 g., and of Na_2HPO_4 as 12.114 g. of anhydrous salt per 100 g. of H_2O at 25°.

[2] Cf. Pallu, *Compt. rend.*, **194**, 458 (1932).

[3] Atkins, *Nature*, **114**, 275 (1924), has studied the phosphates of Ca, Sr, Ba, Mg, Pb, Zn and Ni as regards relationship between solubility and *p*H. In general the amount of salt dissolved rises rapidly with slight increase in acidity.

[4] Apparently a normal phosphate is obtained only in strongly alkaline solution.

[5] Rosenheim, *et al.*, *Ber.*, **48**, 582 (1915); Weinland and Ensgraber, *Z. anorg. allgem. Ch.*, **84**, 340 (1913).

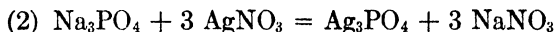
[6] See 6, *d* under the individual metals.

[7] Wunder and Jauneret, *Compt. rend.*, **152**, 1770 (1911).

normal phosphate. A solution of pyrophosphoric acid forms a precipitate with Ag^+, Pb^{++} and Fe^{+3}; no precipitate with Ba^{++}, Ca^{++}, Mg^{++} or Fe^{++}. A solution of metaphosphoric[1] acid precipitates Ag^+ and Pb^{++}, the compounds formed being insoluble in excess of the reagent, soluble in moderately dilute HNO_3. The ions Mg^{++}, Ba^{++}, Ca^{++}, Fe^{++} and Al^{+3} are not precipitated by HPO_3 but Fe^{+3} is precipitated (distinction from H_3PO_4). Orthophosphoric acid — or a phosphate in acetic acid solution — does *not* coagulate egg albumin or gelatine; the same is true of pyrophosphoric acid (distinction from HPO_3).

With Ag^+ soluble orthophosphates form silver orthophosphate,[2] Ag_3PO_4, yellow, darkened on exposure to light; with pyrophosphates, silver pyrophosphate, $Ag_4P_2O_7$, white; and with metaphosphates, silver metaphosphate, $Ag_2(PO_3)_2$, white. All are insoluble in H_2O, soluble in HNO_3 and NH_4OH; $Ag_2(PO_3)_2$ is soluble in an excess of PO_3^- (distinction from $P_2O_7^{-4}$). If an alkali secondary phosphate is added to a neutral solution of Ag^+ the concentration of H^+ is increased and an acid reaction to litmus is induced (Eq. 1), but with the corresponding tertiary phosphate the solution remains neutral (Eq. 2) (distinction between acid and normal phosphates). Strong phosphoric acid (H_3PO_4) gives no precipitate with Ag^+.

$$(1)\ 2\,Na_2HPO_4 + 3\,AgNO_3 = Ag_3PO_4 + 3\,NaNO_3 + NaH_2PO_4$$ [3]

$$(2)\ Na_3PO_4 + 3\,AgNO_3 = Ag_3PO_4 + 3\,NaNO_3$$

A solution of Na_2HPO_4 forms, with Pb^{++}, a white precipitate of $PbHPO_4$, slightly soluble in acetic acid, soluble in NaOH or HNO_3. Lead salts also form white precipitates with $P_2O_7^{-4}$ and PO_3^-; the pyro salt, $Pb_2P_2O_7$, is soluble in excess of $Na_4P_2O_7$. Bismuth salts with PO_4^{-3} form $BiPO_4$, insoluble in water or dilute HNO_3. The primary and secondary salts apparently have not been prepared.

Solutions of orthophosphates give, with Fe^{+3}, Cr^{+3} and Al^{+3}, mostly the normal phosphates, $FePO_4$, $CrPO_4$ and $AlPO_4$. The ferric salt is but slightly soluble in acetic acid. For this reason it is made the basis for separating PO_4^{-3} from ions of Groups III–VI (cf. §148, *d*).[4] The ions Zn^{++}, Mn^{++}, Ba^{++}, Sr^{++}, Ca^{++} and Mg^{++} are precipitated as the secondary or tertiary salt, e.g., $ZnHPO_4$ or $Zn_3(PO_4)_2$, depending upon the acidity of the solvent medium.[5] If it is decidedly alkaline the normal phosphate is obtained, otherwise the secondary salt.[6] In the case of Zn^{++}, Mn^{++} and

[1] Not all of the meta acids give the results stated.

[2] In the presence of $NaC_2H_3O_2$ precipitation will be complete.

[3] Cf. p. 178, also, p. 492, 1.

[4] Cf. Angelescu and Bălănescu, *Kolloid-Z.*, **47**, 207 (1929), *C.A.* **23**, 2867.

[5] For conditions of the formation of the various orthophosphates of Li, Mg, Ca, Zn, Al and Be, see: Travers and Perron, *Ann. ch.*, [10] **1**, 135, 298 (1924); **2**, 43–70 (1924).

[6] It is generally stated that, with Ba^{++} for example, PO_4^{-3} gives $Ba_3(PO_4)_2$ (of course the system must be distinctly alkaline in order to have the PO_4^{-3} present). On the

Mg^{++} conditions may be so adjusted as to quantitatively precipitate these ions as crystalline MNH_4PO_4 which can be ignited to $M_2P_2O_7$ (p. 417, 9).

A solution of a pyrophosphate treated with acetic acid and Cu^{++} or Cd^{++} gives a blue or white precipitate respectively. Zinc acetate gives a white precipitate with $H_4P_2O_7$; luteo cobaltic chloride, $Co(NH_3)_6Cl_3$, gives an orange precipitate with $P_2O_7^{-4}$ (not too dilute), but not from an acetic acid solution. All of these reactions serve to distinguish pyrophosphates from the ortho and meta forms.[1]

With metaphosphoric acid Mg^{++} gives a white precipitate after adding an excess of NH_4OH. The precipitate is soluble in NH_4Cl. Luteo cobaltic chloride forms a brownish-yellow precipitate with PO_3^- in acetic acid solution (distinction from the ortho and pyro acids).

Ammonium molybdate in HNO_3 solution (p. 241, *d*) gives a very delicate test for PO_4^{-3}, through formation of the yellow precipitate of ammonium phosphomolybdate (see below). The reagent reacts but slowly with meta- or pyrophosphates, probably not until they have been converted to the ortho form by the HNO_3 added.

If Sn° or a freshly prepared solution of Sn^{+4}[2] is added to a solution of PO_4^{-3} acidified with HNO_3, the phosphate is precipitated possibly as stannic phosphate, possibly through adsorption by the stannic acid. This reaction is used for the removal of PO_4^{-3} before the precipitation of Group III (§148, p. 365).[3]

B. — **With non-metals and their compounds.** — Phosphoric acid, being a very weak oxidizing agent, is not reduced by any of the reducing acids. Phosphates of Groups I and II are transposed by H_2S, and of the first four groups by alkali sulfides. The metal sulfide remains as a precipitate except in the case of Al and of Cr which form the corresponding hydroxide. Phosphoric acid or an alkali phosphate will be found in the filtrate. The mineral acids HCl, HNO_3 and H_2SO_4 transpose all phosphates; acetic acid reacts similarly except with phosphates of Pb, Al and Fe^{+3}. Sulfurous acid transposes the phosphates of Pb, Ag, Mn, Ca, Ba and Mg. Excess of H_3PO_4 may be used to completely remove all NO_3^-, Cl^- or SO_4^{--} by volatilization as the acid (SO_4^{--} as SO_3) upon evaporation and heating on a sand bath. Sodium carbonate, when boiled with the alkaline earth phosphates, converts each to the corresponding carbonate. The reaction is sufficiently complete for qualitative purposes.[4] Iodine will reduce

other hand a solution of HPO_4^{--} produces a precipitate consisting of a relatively large amount of $BaHPO_4$ and possibly a small amount of $Ba_3(PO_4)_2$. The ion $H_2PO_4^-$ forms no precipitate with the positive ions under consideration. This is the same as saying that the solution is too acid to permit the formation of a precipitate.

[1] For other reactions, see: Rosenheim, *et al.*, *Ber.*, **48**, 582–93 (1915), *C.A.* **9**, 2195.

[2] Gattermann and Schindhelm, *Ber.*, **49**, 2416 (1916), *C.A.* **11**, 766.

[3] Cf. Tarugi, *Boll. ch. farm.*, **61**, 545 (1922), *C.A.* **16**, 4155.

[4] Raquet, *Bull. soc. ch.*, **37**, 1548 (1925), *C.A.* **20**, 719.

phosphates to phosphites, the reaction being proportional to the iodine concentration.[1]

7. Ignition. — Phosphates ignited with Mg° form magnesium phosphide, Mg_3P_2, which on moistening with H_2O forms phosphine, PH_3, readily recognized by its odor.

Orthophosphoric acid, heated to 215°, forms pyrophosphoric acid; when heated to a dull red the meta acid is obtained, which upon further heating sublimes without change. Phosphoric anhydride, P_2O_5, cannot be prepared by ignition of H_3PO_4. Normal orthophosphates, normal pyrophosphates, and metaphosphates of metals whose oxides are not volatile or decomposed by heat alone are unchanged upon ignition. Secondary orthophosphates, $M_2{}^+HPO_4$, are changed to normal pyrophosphates upon ignition. The same is true of normal orthophosphates in which one hydrogen has been replaced by a metallic ion forming a volatile product, e.g., $MgNH_4PO_4$. Primary orthophosphates, $M^+H_2PO_4$, become metaphosphates upon ignition; the same is true of secondary or tertiary orthophosphates having only one hydrogen displaced by a metallic ion whose oxide is non-volatile, e.g., $NaNH_4HPO_4$. Acid pyrophosphates, $M_2{}^+H_2P_2O_7$, upon ignition form metaphosphates. When pyro- or metaphosphates are fused with an excess of a non-volatile oxide, hydroxide or carbonate, the tertiary orthophosphate is formed.

Phosphates of Al, Cr, Fe, Cu, Co, Ni, Mn, Be and U, when raised to a white heat with an alkali sulfate, form oxides of the metals and an alkali tertiary orthophosphate; Phosphates of Ba, Sr, Ca, Mg, Zn and Cd form double phosphates, partial transposition taking place.[2]

8. Detection. — *Ammonium molybdate* will precipitate, preferably from HNO_3 solution, yellow ammonium phosphomolybdate, $(NH_4)_3PO_4 \cdot 12MoO_3$. This is a delicate test for $PO_4{}^{-3}$. It is important that the final system react acid because the precipitate is soluble in a solution containing an excess of OH^-. On the other hand, a large excess of HNO_3 decreases the sensitivity of the test. Ferrocyanides form a red-brown precipitate with the reagent, hence may cause some uncertainty. Halides should be removed with Ag^+ and the test for $PO_4{}^{-3}$ applied to the filtrate. Tartrates and similar organic compounds should be destroyed with concentrated HNO_3 before applying the test. Arsenates are said not to interfere if precipitation is effected in the cold. It is better, however, to remove any $AsO_4{}^{-3}$ with H_2S since a temperature of 30°–40° [3] tends to promote precipitation of the phosphomolybdate.[4] Pyro- and metaphosphoric acids do not give the molybdate test except as they are changed to the ortho acid by the reagents used. Orthophosphates are distinguished from pyro- and

[1] Berthoud and Berger, *J. ch. phys.*, **25**, 568 (1928), *C.A.* **23**, 2092.

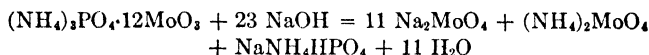
[2] Derome, *Compt. rend.*, **89**, 952 (1879); Grandeau, *Ann. ch. phys.*, [6] **8**, 193 (1886).

[3] If the system becomes too hot MoO_3 will be precipitated. Feigl, *Z. anal. Ch.*, **61**, 454 (1922), *C.A.* **17**, 251, has suggested testing the precipitate with benzidine hydrochloride. If phosphate is present a blue color will appear. Cf. *Ibid.*, **77**, 299 (1929), *C.A.* **23**, 3873.

[4] See: Gutzeit, *Helv. Ch. Acta*, **12**, 713 (1929), *C.A.* **23**, 4645, for various other tests for $PO_4{}^{-3}$. Arnal, *Chimie et industrie*, **20**, 631 (1928), *C.A.* **23**, 576, describes a delicate test depending upon the use of $SbCl_3$ containing an excess of Na_2MoO_4. Lidov, *J. Russ. Phys. Ch. Soc.*, **40**, 817 (1908), *C.A.* **3**, 995, has based a test for $PO_4{}^{-3}$ in rocks on fusion of the sample with Mg°. The magnesium phosphide formed yields PH_3 which will turn $AgNO_3$ or $Cu(C_2H_3O_2)_2$ paper black.

metaphosphates by the color of the precipitate with Ag^+: Ag_3PO_4 is yellow, $Ag_4P_2O_7$ and $Ag_2(PO_3)_2$ are white. Nearly all pyrophosphates[1] are soluble in sodium pyrophosphate, $Na_4P_2O_7$ (distinction from orthophosphates).[2] Sodium metaphosphate does not form a precipitate in a cold, fairly concentrated solution of $ZnSO_4$; with $Na_4P_2O_7$ and $Na_2H_2P_2O_7$ a white precipitate of $Zn_2P_2O_7$ is obtained.[3] HPO_3 can be distinguished from the other phosphoric acids by a test based upon its formation of an insoluble calcium salt.[4]

9. Determination. — Phosphates may be determined *gravimetrically* (*a*) by precipitation as $MgNH_4PO_4$, ignition to $Mg_2P_2O_7$ and weighing as such;[5] (*b*) by precipitation as ammonium phosphomolybdate and weighing as such[6] or conversion of the precipitate to $Mg_2P_2O_7$ which is weighed; or, *volumetrically*, the molybdate may be titrated with standardized NaOH, using phenolphthalein as indicator:

$$(NH_4)_3PO_4 \cdot 12MoO_3 + 23\ NaOH = 11\ Na_2MoO_4 + (NH_4)_2MoO_4 + NaNH_4HPO_4 + 11\ H_2O$$

Other methods have been suggested[7] but they are not widely used.

§238. Sulfur (L. *sulfur*). S = 32.06. Atomic No. 16. Valence 2, 4, 6. Discovery prehistoric.

1. Physical Properties. — Sulfur is polymorphous, existing in various crystalline forms, chiefly rhombic and monoclinic,[8] also in the amorphous state. In addition there are at least two varieties of liquid sulfur, $S\gamma$ and $S\mu$[9] which are said to correspond with S_8 and S_6[10] respectively. Rhombic sulfur, obtained by crystallization from CS_2, has a density of 2.06 at 0° and melts at 112.8° to form $S\gamma$. Monoclinic sulfur, made by crystallization of the liquid S near the melting point, has a density of 1.96 and melts at 119.25° to form $S\gamma$. If the liquid is held for some hours at a temperature only a few degrees above the melting point, then, upon cooling, it solidifies at 114.5°. Below 96° monoclinic sulfur changes to the rhombic form, i.e., monoclinic $\rightleftarrows$ rhombic at 96°. The boiling point of sulfur is 448.5°. The vapor at this temperature is brownish red and consists of S_8 with some S_6 and S_2. If melted sulfur is heated it changes from a mobile, yellow, to a dark red, viscous liquid, the viscosity reaching a maximum at about 200°. Upon further heating, the color darkens almost to black and the fluidity increases appreciably. If, at a temperature near its boiling point, sulfur is poured into cold water, it

[1] For another method of distinguishing pyrophosphates, see: Balareff, *Z. anal. Ch.*, **60**, 385 (1921), *C.A.* **16**, 396.

[2] Cf. Stollenwerk and Bäurle, *Z. anal. Ch.*, **77**, 81 (1929), *C.A.* **23**, 3875.

[3] Knorre, *Z. angew. Ch.*, **5**, 639 (1892).

[4] Cf. Holt and Myers, *J. Ch. Soc.*, **103**, 532 (1913). For another differentiating test, see: de Boer, *Ch. Weekblad*, **21**, 561 (1924), *C.A.* **19**, 799.

[5] For a good discussion of this method, see: Epperson, *J. Am. Ch. Soc.*, **50**, 328 (1928).

[6] Posternak, *Compt. rend.*, **170**, 930 (1920), *C.A.* **14**, 2306, has studied the variations in composition of the phosphomolybdate. Cf. Epperson, *loc. cit.*

[7] See: Hillebrand and Lundell, p. 556 *et seq.*

[8] Several others have been reported but are of minor importance. Cf. Mellor, X, p. 23 (1930); Friend, VII, II, p. 14 (1931).

[9] Cf. Hammick and Zvegintzov, *J. Ch. Soc.*, **1930**, 273.

[10] Cf. Ephraim, p. 80. He states that S_μ corresponds to S_4.

forms a soft, ductile elastic mass (S_6) resembling rubber. In a few hours this ductile sulfur changes back to the ordinary rhombic form which is the stable state at room temperatures. This change is accompanied by the evolution of heat. If liquid sulfur at about 112° is poured into water it forms ordinary, brittle sulfur. In contact with air sulfur ignites at 248°. It burns with a pale blue flame to SO_2, which has a penetrating odor. Sulfur is distinctly a non-metal. In chemical activity, volatility and other properties it is intermediate between oxygen and selenium as indicated by its position in the periodic table.

2. Occurrence. — Sulfur is found native; as SO_2 in volcanic districts; as H_2S in some mineral waters; as the sulfide, iron pyrites (FeS_2), copper pyrites ($CuFeS_2$), realgar (AsS), orpiment (As_2S_3), zinc blende (ZnS), cinnabar (HgS), galena (PbS), etc.; as sulfate in gypsum ($CaSO_4 \cdot 2H_2O$), barite ($BaSO_4$), etc. For many years Italy, including Sicily, produced the major portion of the world's supply of sulfur. More recently the quantity from that source has dwindled, until in 1929 the Italian output amounted to less than one-tenth of that of the United States. During the year mentioned domestic shipments totaled slightly over 2.4 million long tons, 99% of which came from Texas. Concerning pyrites, an equally important source of sulfur, in 1928 there were mined 7.3 million tons of which Spain produced one-half, Norway one-tenth, Japan and Italy each, one-twelfth, and Germany, France and the United States the major portion of the balance. During 1929 there were used in the United States about 1.6 million tons of sulfur. The heavy chemical industry consumed one-third; fertilizers and insecticides accounted for slightly less than one-third, and about one-fifth went to make pulp and paper.[1] The average price for sulfur, analyzing 99% or better, has for some years been $18 per ton at the mine.

3. Preparation. — *a.* In Texas sulfur is mined by the Frasch process.[2] Holes are drilled down to the sulfur deposit, about 700 feet; then in each hole three pipes are placed concentrically. The outer, six-inch pipe conveys hot water (180°) under pressure down to the bottom of the hole where the temperature of the sulfur is soon raised slightly above its melting point. It is then forced up through the middle, three-inch pipe, by compressed air pumped in through the innermost, one-inch pipe. The sulfur flows out into bins where it solidifies in huge cakes, each containing many tons. Refining is unnecessary. *b.* Iron pyrites may be heated in closed retorts: $3\ FeS_2 = Fe_3S_4 + S_2$; or at a higher temperature: $2\ FeS_2 = 2\ FeS + S_2$. Some years ago much of the sulfur in pyrites was converted into and utilized as sulfuric acid, but nowadays practically all of this acid is made from elemental sulfur.[3]

4. Hydrides, Oxides and Acids. — Sulfur forms one[4] important hydride, hydrosulfic acid, H_2S (§239), obtained as a gas by treating a sulfide (usually FeS) with a dilute acid (not HNO_3). Sulfur and oxygen combine directly to form sulfur dioxide, SO_2, (§242) which, with the aid of a catalyst, will combine with an additional atom of oxygen to form sulfur trioxide, SO_3 (§243). Sulfur sesquioxide, S_2O_3, has been prepared by dissolving sulfur in sulfur dioxide.[5] Another oxide, also of minor importance, is the heptoxide, S_2O_7, obtained by the action of the electric discharge on SO_3 and O. The acids[6] of sulfur are given in Table 43; those of greater importance will be considered in the succeeding sections. As regards acid strength these acids have been arranged as follows, the weakest being placed first: H_2S, H_2SO_3, H_2SO_4, $H_2S_2O_3$, $H_2S_2O_4$, $H_2S_2O_6$.[7]

[1] For other uses see: Friend, VII, II, p. 12.

[2] A good description is to be found in Muspratt, Suppl. Vol. II, 2, p. 979 (1927); also in *J. Ch. Education*, **6**, 129 (1929).

[3] Sufficient sulfuric acid to supply all needs could probably be made from the SO_2 allowed to escape into the air during the smelting of various sulfide ores. In some cases, particularly where objection has been raised because of its destructive action on vegetation, the SO_2 is now utilized as indicated above. See: Cobleigh, *Ind. Eng. Ch.*, **24**, 717 (1932).

[4] The persulfides, H_2S_2, H_2S_3, H_2S_5, etc., merit no consideration here. See: Mills and Robinson, *J. Ch. Soc.*, **1928**, 2326.

[5] Cf. Vogel and Partington, *J. Ch. Soc.*, **127**, 1514 (1925).

[6] Cf. Ephraim, p. 453, *et seq.*; Caven and Landers, p. 283, *et seq.*

[7] Kolthoff, *Rec. trav. ch.*, **43**, 216 (1924), *C.A.* **18**, 2455.

5. Solubilities. — The various kinds of sulfur are insoluble in water. Ordinary (not precipitated) sulfur is soluble in carbon disulfide. At 25° the monoclinic is 1.3 times as soluble as the rhombic form. The ductile variety is insoluble. Samples of commercial sulfur are seldom found which are entirely soluble or insoluble in CS_2. Forms of sulfur insoluble in that medium are made soluble by heating to the melting point. Amorphous sulfur (formed by adding an acid to a thiosulfate or SO_2 to a solution of H_2S), insoluble in CS_2, is changed to the soluble form by mixing with a solution of H_2S water. It dissolves readily in a hot solution of NaOH or $Ca(OH)_2$, forming polysulfides and thiosulfates: $3\ Ca(OH)_2 + 12\ S = 2\ CaS_5 + CaS_2O_3 + 3\ H_2O$. These can be separated by alcohol, in which the sulfides dissolve. These products are also readily decomposed by acids with separation of sulfur.[1] Sulfur is readily soluble in solutions of the alkali sulfides, polysulfides being formed: $(NH_4)_2S + (x - 1)S = (NH_4)_2S_x$. The solution changes in color from a pale yellow to a deep red as the value of x increases. Precipitated sulfur, as obtained in the course of analysis when HCl is added to the $(NH_4)_2S_x$ extract in Group II, is soluble in benzol or low boiling petroleum ether. This is of value when looking for traces of As or Sb sulfides.[2]

TABLE 43

SULFUR ACIDS

Hydrosulfic acid	H_2S	H.S.H*
Sulfoxylic acid†	H_2SO_2	$H.SO_2.H$
Hyposulfurous acid†	$H_2S_2O_4$	$H.SO_2.SO_2.H$
Sulfurous acid	H_2SO_3	$HO.SO_2.H$
Sulfuric acid	H_2SO_4	$HO.SO_2.OH$
Pyro- or disulfuric acid	$H_2S_2O_7$	$HO.SO_2.O.SO_2.OH$
Permonosulfuric acid‡	H_2SO_5	$H.SO_2.O.SO_2.H$
Persulfuric acid	$H_2S_2O_8$	$HO.SO_2.O.O.SO_2.OH$
Thiosulfuric acid†	$H_2S_2O_3$	$HS.SO_2.OH$
Dithionic acid	$H_2S_2O_6$	$HO.SO_2.SO_2.OH$
Trithionic acid	$H_2S_3O_6$	$HO.SO_2.S.SO_2.OH$
Tetrathionic acid	$H_2S_4O_6$	$HO.SO_2.S.S.SO_2.OH$
Pentathionic acid	$H_2S_5O_6$	$HO.SO_2.S.S.S.SO_2.OH$
[Hexathionic acid]†	$H_2S_6O_6$	$HO.SO_2.S.S.S.S.SO_2.OH$

* The formulas in this column merely suggest that there is an order to the sulfur acids. For electronic formulas, see: Caven and Landers, p. 488–91; Bassett and Durant, *J. Ch. Soc.*, **1927,** 1444. Noyes and Steinous, *J. Am. Ch. Soc.*, **51,** 1409 (1929), footnote, have suggested a "rational" nomenclature for the sulfur acids.
† Salts have been prepared but not the free acid.
‡ Caro's acid.

6. Reactions. — *A.* **With metals and their compounds.** — Sulfur does not combine with metals without the aid of heat except that under very great pressure it unites with Pb, Sn, Sb, Bi, Cu, Cd, Fe, Zn and Mg. When heated, sulfur combines with all metals except Au, Pt, Ir and Be. If heated with many of the metal oxides (PbO, HgO, CdO, etc.) sulfur is changed to sulfide and sulfate: $4\ PbO + 4\ S = 3\ PbS + PbSO_4$.

"Flowers of sulfur"[3] boiled with $SnCl_2$ give SnS and $SnCl_4$; with $Hg_2(NO_3)_2$ one-half of the Hg is precipitated as HgS. There is no action with the sulfates of Cd, Fe^{++}, Mn^{++}, Ni and Zn; or with a solution of

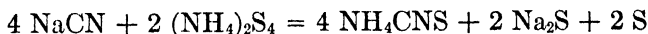
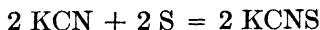
[1] Method used for preparation of "precipitated" sulfur.
[2] Fresenius, *Z. anal. Ch.*, **33**, 573 (1894).
[3] Sulfur obtained by sublimation.

Sb^{+3}, Bi^{+3}, AsO_3^{-3} or AsO_4^{-3}. Sulfur boiled with the hydroxide of K,[1] Na, NH_4, Ba, Sr, Ca, Mg, Co, Ni, Mn, Hg_2^{++}, Hg^{++}, Bi, Cu_2^{++}, Cu^{++}, Cd, Pb, or Ag forms a sulfide and a thiosulfate, also some sulfate. There is no action with the hydroxides of Fe, Zn and Sn.[2]

B. **With non-metals and their compounds.**

1. *HCN* warmed with sulfur or a polysulfide becomes a thiocyanate:

$$2\ KCN + 2\ S = 2\ KCNS$$

$$4\ NaCN + 2\ (NH_4)_2S_4 = 4\ NH_4CNS + 2\ Na_2S + 2\ S$$

2. *Nitric acid* reacts with S to form NO and H_2SO_4. Concentrated acid and long boiling are necessary for the complete oxidation of the sulfur. The crystallized variety is attacked more slowly than the amorphous or sublimed.

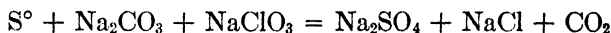
3. *Red phosphorus* readily unites with S at room temperature, forming P_2S_3 or P_2S_5, depending upon the relative amounts of the elements used. White phosphorus combines explosively. Tertiary sodium or potassium phosphate, when boiled with sulfur, forms an alkali polysulfide and thiosulfate, changing the phosphate to a secondary salt.

4. *Sulfuric acid,* concentrated and hot, reacts with S to form SO_2: $4\ H_2SO_4 + 2\ S = 6\ SO_2 + 4\ H_2O$. Sulfur trioxide, when added to S at 12°, forms the blue sulfur sesquioxide, S_2O_3 (apparently not the anhydride of hyposulfurous acid). Sulfurous acid reacts with sulfur even at room temperature, forming thiosulfuric acid and tri- or tetrathionic acid.[3]

5. *Chlorine* in the presence of H_2O reacts with S to form HCl and H_2SO_4. $HClO_3$ yields the same products. The same sort of reaction takes place with Br° and $HBrO_3$. Sulfur does not appear to have any action upon iodine or upon iodine compounds. Hydriodic acid, HI, however, is said to reduce S° to S^{--}.

7. **Ignition.** — In the air at 248° sulfur begins to oxidize rapidly to SO_2, burning with a blue flame. When fused with the following elements sulfur unites with them to form sulfides: Pb, Ag, Hg, Sn, As, Sb, Bi, Cu, Cd, Zn, Co, Ni, Fe, Sr, Ca, Mg, K, Na, In, Tl, Pt, Pd, Rh, Ir, Li, Ce, La, Ne, Pr. Free sulfur, or any compound containing sulfur with valence less than six, is oxidized to a sulfate when fused with Na_2CO_3 and an alkali nitrate or chlorate, nitric oxide or a chloride being formed and CO_2 escaping:

$$S^\circ + Na_2CO_3 + NaClO_3 = Na_2SO_4 + NaCl + CO_2$$

$$S^\circ + 2\ NaNO_3(+ Na_2CO_3) = Na_2SO_4 + 2\ NO$$

[1] Tartar, *J. Am. Ch. Soc.*, **35**, 1741 (1913), gives as the primary reaction: $6\ KOH + 8\ S = 2\ K_2S_3 + K_2S_2O_3 + 3\ H_2O$. The K_2S_3 combines with two more atoms of sulfur to form K_2S_5.

[2] Senderens, *Bull. soc. ch.* [3] **6**, 800 (1891).

[3] Colefax, *J. Ch. Soc.*, **61**, 199 (1892).

8. Detection. — Sulfur is detected by (*a*) burning in air to form SO_2 of characteristic odor; (*b*) its solubility in CS_2; (*c*) the formation of a sulfate with oxidizing agents; (*d*) the formation of sulfides upon fusion with a metal (Fe° is often used); (*e*) the blackening of a silver coin after boiling with NaOH; (*f*) the formation of a purple color with sodium nitroferricyanide after boiling with NaOH.

9. Determination. — Sulfur is usually determined by conversion to $BaSO_4$ which may be weighed or, if only a small amount is involved, estimated by means of a sulfur "photometer." *Volumetrically*, sulfur may be converted to a sulfate which is precipitated as benzidine sulfate and titrated with standardized NaOH using phenolphthalein as an indicator.

§239. Hydrosulfic Acid. H_2S

1. Physical Properties. — Hydrosulfic acid, as a solid, melts at − 83°; the liquid boils at − 60.2° under 760 mm. pressure; one liter of the gas at S.T.P. weighs 1.539 g.[1] In the liquid or gaseous state there is apparently no polymerization. Under ordinary conditions H_2S is a colorless, poisonous gas, burning readily to form sulfur dioxide and water: $2\ H_2S + 3\ O_2 = 2\ SO_2 + 2\ H_2O$. If insufficient oxygen is present, sulfur will also be formed. Dry H_2S is stable but an aqueous solution slowly decomposes upon exposure to the air with separation of sulfur. The presence of finely divided Ni° markedly hastens the reaction. The gas is readily expelled from its aqueous solution by boiling. Both the gas and its water solutions have a feebly acid reaction toward moist litmus paper. They also possess a characteristic odor resembling that of bad eggs. In acid or in alkaline solution H_2S is a strong reducing agent.

2. Occurrence. — Hydrogen sulfide is found free in volcanic gases and frequently in mineral springs. While the inhaled gas is poisonous,[2] the mineral water containing it is reported to be a healthful beverage.

3. Preparation. — For laboratory purposes H_2S is nearly always made by adding dilute H_2SO_4 or HCl to FeS: $FeS + H_2SO_4 = FeSO_4 + H_2S$. Concentrated H_2SO_4 has no action on FeS unless heated, and then SO_2 is evolved: $2\ FeS + 10\ H_2SO_4 = Fe_2(SO_4)_3 + 9\ SO_2 + 10\ H_2O$. The common impurities in H_2S are hydrogen and arsine. The former may come from metallic iron in the FeS, the latter from arsenic in the sulfide or the acid. A better H_2S may be obtained by saturating H_2O containing a suspension of $Mg(OH)_2$ with H_2S. Upon heating the mixture pure H_2S is evolved.[3] A good quality of H_2S may also be prepared by dropping H_2O on Al_2S_3.[4] Mixtures of sulfur and various organic compounds when warmed give off H_2S, e.g., paraffin and S°,[5] vaseline and S°, etc. Under certain conditions this method is very convenient since the evolution of gas is easily controlled by regulating the temperature.

5. Solubilities. — At 20° and 760 mm. one volume of water dissolves 2.9[6] volumes of H_2S, which gives a solution about 0.26 *N*. Sulfides of the alkalis are soluble in water, all others insoluble.[7] Many metal sulfides

[1] Baume and Perrot, *J. ch. phys.*, **6**, 610 (1908).

[2] In the laboratory H_2S is potentially one of the more dangerous poisons due chiefly to a lack of appreciation of its toxicity, the fact that it is a gas easily distributed and that frequent usage leads to laxity regarding precautions.

[3] Cardoso, *Gazz. ch. ital.*, **51**, I, 153 (1921). For preparation of highest quality H_2S see: Moissan, *Compt. rend.*, **137**, 363 (1903).

[4] Fronzes-Diagon, *Bull. soc. ch.*, [4] **1**, 36 (1907).

[5] Henwood, *et al.*, *J. Franklin Inst.*, **199**, 685 (1925).

[6] Corrected to S.T.P. Cf. Mellor, X, 131.

[7] For a detailed discussion of the solubility of sulfides see: **Part I, p. 98–114.**

hydrolyze in the presence of water; in general H_2S and the hydroxide of the metal are formed.

Sulfides that dissolve in dilute H_2SO_4 evolve H_2S, e.g., CdS, FeS, MnS, ZnS, etc. If a sulfide requires concentrated H_2SO_4 for its solution, S and SO_2 are formed,[1] e.g., Bi_2S_3, CuS, HgS. If concentrated H_2SO_4 is used upon a sulfide that might have been dissolved in dilute acid no H_2S is evolved: $ZnS + 4\ H_2SO_4 = ZnSO_4 + 4\ SO_2 + 4\ H_2O$. With a small amount of H_2O present, the reaction becomes: $ZnS + 2\ H_2SO_4 = ZnSO_4 + S + SO_2 + 2\ H_2O$. Mercuric sulfide is practically insoluble in hot, dilute (2 *N*) HNO_3. A more concentrated acid may form the slightly soluble, white, double salt, $2HgS \cdot Hg(NO_3)_2$. Mercuric sulfide is readily soluble in hypochlorites, aqua regia, chloric acid or dilute HCl containing H_2O_2. Practically all of the other sulfides are soluble in HNO_3. Many are also dissolved upon treatment with Zn° and dilute HCl. Long continued boiling with water more or less completely decomposes the sulfides of Ag, As, Sb, Sn, Fe, Co, Ni and Mn; sulfides of the following are unaffected: Hg, Au, Pt, Mo, Cu, Cd and Zn.

As a reagent, hydrosulfic acid, gaseous or in solution, finds extended application in the analytical laboratory. The grouping of the metals for analysis depends very largely upon the relative concentration of sulfide ion required to precipitate them.[2, 3]

The sulfides of the first four groups are insoluble in water. Hydrosulfic acid precipitates ions of the metals of Groups I and II in acid,[4] neutral or alkaline[5] solution. (Arsenic is the most important exception to this rule.

[1] In some cases only SO_2.

[2] Padoa and Cambi, *Gazz. ch. ital.*, **37**, II, 111 (1907), *C.A.* **2**, 1243, have approximately determined the minimum amount of H_2S required to form visible precipitates in dilute solutions of Cd^{++}, Zn^{++} and Fe^{++} in the presence of varying $[H^+]$.

[3] From a theoretical standpoint the mechanism of the precipitation of sulfides has not been satisfactorily explained, the very low concentration of S^{--} being an important difficulty. Cf. Part I; Smith and Semon, *J. Am. Ch. Soc.*, **46**, 1325 (1924); Feigl, *Z. anorg. allgem. Ch.*, **57**, 251 (1926), *C.A.* **21**, 1423. For a consideration of the equilibria in the precipitation of metals by H_2S, see: Bruner and Zawadski, *Z. anorg. allgem. Ch.*, **65**, 136 (1910), *C.A.* **4**, 980; **67**, 454, *C.A.* **4**, 2758. Padoa and Cambi, *Atti accad. Lincei*, [5] **15**, ii, 787 (1906), have discussed various factors in the precipitation with H_2S; cf. Dede and Bonin, *Ber.*, **55B**, 2327 (1922), *C.A.* **16**, 4155, for a consideration of the action of neutral chlorides in preventing precipitation by H_2S. For an exhaustive study of the behavior of some metal sulfides in the presence of alkali sulfides, see: Ditte, *Ann. ch. phys.*, [8] **12**, 229 (1907), *C.A.* **2**, 237. Concerning the use of S^{--} in analysis, also the properties of various sulfides, see: Cattelain, *J. pharm. ch.*, [8] **12**, 367 (1930).

[4] Pb^{++} is only partially precipitated by H_2S in a solution much over 0.5 *N* with HCl. The same is true with Cd^{++} and Sn^{++}. Whether this is due to a lowering of the S^{--} by common ion effect or to the formation of a complex ion, as $PbCl_4^{--}$, $CdCl_4^{--}$, etc., has not been fully decided.

[5] Zn^{++} is precipitated incompletely by a solution of NH_4OH saturated with H_2S. The same reagent diluted with an equal volume of NH_4OH, i.e., containing S^{--} instead of HS^-, gives a satisfactory separation.

It is not precipitated unless some free acid, or salt that is not alkaline to litmus, is present.) The product is a sulfide, but Hg_2^{++} forms HgS and Hg, and AsO_4^{-3} may form a mixture of As_2S_5, As_2S_3 and S. Ferric iron is reduced to ferrous with liberation of S°. In acid solution other third and fourth group ions, in the tervalent and divalent states respectively, are not disturbed except by "coprecipitation" (e.g., if HgS is precipitated from an acid solution containing Zn^{++} or Cd^{++} it always carries down some of these ions; tin precipitated in the presence of Co^{++} almost invariably carries down some of that ion).[1]

Soluble sulfides transpose salts of the first four[2] groups. The product is a sulfide except that with Al^{+3} and Cr^{+3} it is the hydroxide; mercurous salts form HgS + Hg; Fe^{+3} in acid solution becomes Fe^{++}, in an alkaline solution Fe_2S_3.

The precipitated sulfides have strongly marked colors: ZnS is white; MnS, flesh;[3] PbS, CuS, FeS and Fe_2S_3 are black; As_2S_3, As_2S_5, SnS_2 and CdS are yellow; Sb_2S_3, orange; SnS, brown; HgS forms complexes with the unaffected $HgCl_2$ of the sort xHgS·$y$$HgCl_2$ which vary in color from white through yellow, orange and brown to black, as the value of x increases and y decreases.

6. Reactions. — *A.* **With metals and their compounds.**[4] Some metals are converted into sulfides when exposed to moist H_2S, e.g., Ag°, Cu°, Hg°, etc.:[5] $4\ Cu + 2\ H_2S + O_2 = 2\ Cu_2S + 2\ H_2O$. The alkali polysulfides slowly attack many metals with formation of sulfides: Sn° becomes $M_2{}^+SnS_3$; Ag° forms Ag_2S (no action with colorless $(NH_4)_2S$); Ni° forms NiS; Fe° yields FeS; Cu° changes to CuS and Cu_2S (with colorless $(NH_4)_2S$, Cu_2S and H_2 are said to result).

The hydroxides and non-ignited oxides[6] of Pb^{++}, Ag, Hg^{++}, Sb, Sn, Bi^{+3}, Cu, Cd, Fe^{++}, Co^{++}, Ni^{++}, Mn^{++}, Zn, Ba, Sr, Ca, Mg, K, Na and NH_4^+ unite with moist H_2S at room temperature to form sulfides without changing the valence of the metal. In other cases the valence is changed, usually with liberation of sulfur. Dry H_2S has no action on the dry salts of Pb, Ag, Hg, As, Sb, Sn, Bi, Cu, Cd or Co. The freshly precipitated

[1] An interesting variation of the difficulties encountered in this field is described by Feigl, *Z. anal. Ch.*, **65**, 25 (1924). He shows that whereas MnS is readily soluble in acetic acid, a mixture of MnS and ZnS upon digestion with this acid leaves a residue of ZnS containing up to 24% MnS. Cf. Tubandt and Reinhold, *Z. physik. Ch.*, **140**, 291 (1929).

[2] Sulfides of Group V metals may be precipitated under certain conditions (p. 399, *e*), but readily undergo hydrolysis.

[3] This form, obtained by rapid precipitation, differs in particle size and crystalline structure from the more stable, green modification. Cf. Mellor, XII, 389; Weiser and Milligan, *J. Phys. Ch.*, **35**, 2330 (1931).

[4] See division 6, *e* under the individual metals, also division 5 above.

[5] For a study of the reaction $M° + H_2S = MS + H_2$, see: Jellinck and Zakowski, *Z. anorg. allgem. Ch.*, **142**, 1 (1925).

[6] The hydroxides generally react more readily than the oxides.

sulfide of any metal will precipitate any other metal ion if the latter forms a sulfide of lower solubility. The higher valences of Cr and Mn react with H_2S to give a variety of products depending largely on the acidity and temperature. An aqueous solution of Na_2CrO_4 forms $Cr(OH)_3$, S°, Na_2S and $Na_2S_2O_3$;[1] with a dichromate in the presence of sufficient HCl the reaction is: $K_2Cr_2O_7 + 3\ H_2S + 8\ HCl = 2\ CrCl_3 + 2\ KCl + 3\ S° + 7\ H_2O$. An aqueous solution of $KMnO_4$ (1%) reacts with H_2S as follows: $10\ KMnO_4 + 22\ H_2S = 3\ K_2SO_4 + 10\ MnS + 2\ K_2S_2O_3 + 5\ S° + 22\ H_2O$.[2]

B. **With non-metals and their compounds.**

1. *$H_3Fe(CN)_6$* reacts with H_2S to form $H_4Fe(CN)_6$ and S°.
2. *HNO_3* forms NO and S. If the HNO_3 is hot and concentrated the sulfur is oxidized to H_2SO_4.
3. *H_2O_2* slowly acts upon H_2S to form S°. In alkaline solution oxidation to SO_4^{--} takes place readily.
4. *H_2S* has no reducing action on the acids of phosphorus.
5. *H_2SO_3* forms pentathionic acid, $H_2S_5O_6$[3] and S°: $5\ H_2SO_3 + 5\ H_2S = H_2S_5O_6 + 5\ S + 9\ H_2O$. An excess of H_2S produces only S°: $H_2SO_3 + 2\ H_2S = 3\ S + 3\ H_2O$. Dilute H_2SO_4 has no action on H_2S. If the acid is hot and concentrated, S° and SO_2 are formed: $H_2SO_4 + H_2S = S° + SO_2 + 2\ H_2O$.
6. *Chlorine*, with H_2S in excess, forms HCl and S°. With Cl° in excess, the products are HCl and H_2SO_4. $HClO_3$, with H_2S in excess, forms HCl and S; with $HClO_3$ in excess, HCl and H_2SO_4. The same is true in the case of Br° and $HBrO_3$, the corresponding bromine compounds being formed instead of those of chlorine as indicated. Iodine and HIO_3[4] form only HI and S°.

7. **Ignition.** — Dry H_2S is not decomposed when heated to 350°–360°. At this temperature AsH_3 is decomposed in the presence of K_2S_3, "liver of sulfur": $2\ AsH_3 + 3\ K_2S_3 = 2\ K_3AsS_3 + 3\ H_2S$. This furnishes a ready means of purifying H_2S for toxicological work (cf. 3 above).

If air is excluded some sulfides may be sublimed unchanged, e.g., HgS, As_2S_3, As_2S_5, Sb_2S_3, etc. In some cases partial decomposition takes place leaving a sulfide of a lower metallic valence: $FeS_2 = FeS + S°$. Some sulfides remain unchanged upon ignition in absence of air, e.g., FeS, MnS, CdS, etc. All sulfides undergo some change on being ignited in air; Sb_2S_3, CuS, Al_2S_3, Cr_2S_3, etc., evolve SO_2 and leave the oxide of the metal; HgS, Ag_2S, etc., evolve SO_2 and leave the free metal. All sulfides, when fused with Na_2CO_3 and $NaNO_3$ or $KClO_3$, are oxidized to an alkali sulfate, the metallic radical forming a carbonate, oxide or free metal. When ignited on charcoal with Na_2CO_3 or fused with this latter reagent in a porcelain crucible (distinction from sulfates), soluble sodium sulfides are obtained. The sulfide is readily detected through the formation of a

[1] Dunnicliff and Soni; *J. Phys. Ch.*, **33**, 81 (1929).
[2] Foerster and Vogel, *Z. anorg. allgem. Ch.*, **155**, 161 (1926).
[3] Cf. Heinze, *J. prakt. Ch.*, **99**, 109 (1919), *C.A.* **14**, 26, who has tried to determine the products more exactly.
[4] Dean, *J. Am. Ch. Soc.*, **40**, 619 (1918), has shown that a large excess of KIO_3 oxidizes S^{--} to SO_4^{--} provided sufficient HCl is present to prevent hydrolysis of the ICl formed.

black spot on a silver[1] coin when a portion of the melt is placed on the coin and moistened. Heavy metal sulfides may be reduced readily by ignition with metallic aluminum.[2]

8. Detection. — The characteristic odor of H_2S is perceptible in the air when one part in 700,000 is present. A piece of filter paper moistened with lead acetate solution turns black when exposed to H_2S.[3] A drop or two of NH_4OH on the paper, or the use of Na_2PbO_2 in place of $Pb(C_2H_3O_2)_2$, is said to greatly increase the delicacy of the test.[4] Sodium nitroferricyanide, $Na_2NOFe(CN)_5$, gives a very delicate and characteristic test for a sulfide in alkaline solution through the formation of a transient purple color.[5] If a soluble or insoluble sulfide is treated with a solution of sodium azide, NaN_3, and iodine, nitrogen will be evolved on heating. This is said to be a very delicate test for a sulfide.[6, 7]

9. Determination. — *Gravimetrically*, sulfide sulfur may be determined by oxidation to sulfate and precipitation as $BaSO_4$ which is weighed. The oxidation may be effected by (*a*) fusion with Na_2CO_3 and $NaNO_3$ or $KClO_3$ or with Na_2O_2; (*b*) evolution of the sulfide as H_2S which is absorbed in ammoniacal perhydrol; (*c*) treatment with hot concentrated HNO_3. The *volumetric* determination of sulfide has been especially developed in the iron and steel industry. There the sample is dissolved in HCl and the evolved H_2S is absorbed in ammoniacal $CdCl_2$ or $ZnSO_4$. After acidification the solution is titrated with standardized iodine or iodate:

$$H_2S + I_2 = 2\,HI + S \quad \text{or}$$

$$3\,H_2S + KIO_3 + 6\,HCl + 5\,KI = 6\,HI + 3\,S + 6\,KCl + 3\,H_2O$$ [8]

In the more general case sulfides may be titrated by the well-known iodide-thiosulfate procedure or by treatment with a known quantity of an oxidizing agent which will convert the sulfide to sulfate followed by titration of the excess oxidant.[9]

[1] For the course of the reaction between Ag and sulfides ("hepar" test), see: Hahn, *Z. anorg. allgem. Ch.*, **99**, 118 (1917), *C.A.* **11**, 3184.

[2] Paravano and Agostini, *Gazz. ch. ital.*, **49**, I, 103 (1919).

[3] Schneider, *Z. anal. Ch.*, **22**, 81 (1883). Cf. McBride and Edwards, B. Stds. Tech. Paper, **41** (1914), *C.A.* **9**, 520.

[4] Truesdale, *Ind. Eng. Ch., Anal. Ed.*, **2**, 299 (1930), reports a positive test with 1.5×10^{-9} g. of H_2S.

[5] The formula for the colored compound has not been settled. Pavolini, *Boll. ch. farm.*, **69**, 713, 719 (1930), *C.A.* **25**, 2934, says that the color is due to colloidal Berlin blue. Scagliarini and Pratesi, *Atti accad. Lincei*, [6] **8**, 75 (1928), *C.A.* **23**, 573, believe that the formula usually given, $Na_2Fe(CN)_5NO \cdot Na_2S$, is incorrect, that the N and S are directly connected, giving N-S-R.

[6] Feigl, *Z. anal. Ch.*, **74**, 369 (1928).

[7] For comparisons of the various tests for S^{--}, see: Truesdale, *loc. cit.*; Gutzeit, *Helv. Ch. Acta*, **12**, 713 (1929), *C.A.* **23**, 4645; Wilmet, *Compt. rend.*, **184**, 287 (1927).

[8] Cf. Lundell, Hoffman and Bright, p. 232, *et seq.* Pulsifer, "The Determination of Sulfur in Iron and Steel," Easton, Pa., The Chemical Publishing Co., **1922**. An extensive bibliography is included.

[9] Hypobromite has been suggested by Willard and Cake, *J. Am. Ch. Soc.*, **43**, 1610 (1921). Iodine has been recommended by Kjerrman, see Lundell, Hoffman and Bright, p. 238, footnote. Calcium hypochlorite ("H.T.H.") is equally satisfactory. H_2S may be absorbed in a solution of this reagent and the excess determined by titration. For other methods see: Rüdisüle VII, p. 740, *et seq.*

Colorimetrically, small amounts of sulfide may be determined by means of the methylene blue test.[1]

§240. Thiosulfuric Acid. $H_2S_2O_3$

1. Physical Properties. — Thiosulfuric acid, $H_2S_2O_3$ (formerly called hyposulfurous acid),[2] has not been isolated; but it probably is formed when a weak acid is added to a solution of sodium thiosulfate, $Na_2S_2O_3$. Decomposition soon begins, however, with formation of H_2SO_3 and S°. The thiosulfates are not particularly stable compounds, some decomposing shortly after formation, e.g., mercury thiosulfates. Alkali thiosulfates decompose upon heating into sulfate and polysulfide: $4\ Na_2S_2O_3 = 3\ Na_2SO_4 + Na_2S_5$. Other salts give H_2S and S° in addition. When boiled a solution of $S_2O_3^{--}$ forms SO_4^{--} and H_2S or a sulfide of the metal involved. The most extensive uses for thiosulfates, particularly the sodium salt, are in photography and as an "antichlor" in bleaching cloth.

3. Preparation. — Thiosulfates are prepared by boiling sulfur in a solution of normal alkali sulfite: $Na_2SO_3 + S = Na_2S_2O_3$. Fixed alkali or alkaline earth hydroxides react with sulfur to form thiosulfates: $3\ Ca(OH)_2 + 12\ S = 2\ CaS_5 + CaS_2O_3 + 3\ H_2O$. It is possible to prepare $Na_2S_2O_3$ by the interaction of NaHS and $NaHSO_3$:

$$2\ NaHS + 4\ NaHSO_3 = 3\ Na_2S_2O_3 + 3\ H_2O$$

The product is very pure if the concentration of H^+ is properly controlled.[3]

5. Solubilities. — The larger number of thiosulfates are soluble in water; those of Ba,[4] Pb and Ag are only slightly soluble. The thiosulfates are insoluble in alcohol. They are decomposed by acids with the production of S°.

Alkali thiosulfate solutions dissolve the thiosulfates of Pb and Ag; also AgCl, AgBr, AgI, Hg_2Cl_2, PbI_2, $PbSO_4$, $CaSO_4$ and some other compounds by formation of double thiosulfates:

$$Ag_2S_2O_3 + Na_2S_2O_3 = 2\ NaAgS_2O_3$$

$$AgCl + Na_2S_2O_3 = NaAgS_2O_3\ ^{5} + NaCl$$

$$PbSO_4 + 3\ Na_2S_2O_3 = Na_4Pb(S_2O_3)_3 + Na_2SO_4$$

6. Reactions. — *A*. **With metals and their compounds.** — Pb^{++} and Ag^+ are precipitated by $S_2O_3^{--}$ as white thiosulfates, soluble in excess of the reagent. These precipitates decompose upon standing, rapidly if warmed, into sulfides and H_2SO_4:

$$Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4\ ^{6}$$

$$2\ PbS_2O_3 + H_2O = PbS + PbS_3O_6\ ^{7}$$

[1] Mecklenburg and Rosenkränzer, *Z. anorg. allgem. Ch.*, **86**, 146 (1914).
[2] Hence the term "hypo" used by photographers for $Na_2S_2O_3$.
[3] Foerster and Mommsen, *Ber.*, **57B**, 258 (1924), *C.A.* **18**, 1254.
[4] Authenrieth and Windaus, *Z. anal. Ch.*, **37**, 290 (1898).
[5] Other complexes are also formed as $Ag_2S_2O_3 \cdot 2Na_2S_2O_3$, etc.
[6] Cf. Hackl, *Ch. Ztg.*, **47**, 210, 266 (1923); Perkins and King, *J. Ch. Soc.*, **103**, 300 (1913).
[7] The reaction is apparently reversible. Fogh, *Compt. rend.*, **110**, 524 (1890).

Hg^{++} forms a white precipitate with $S_2O_3^{--}$, that almost instantly decomposes to form black HgS.[1] Mercurous chloride dissolves in $S_2O_3^{--}$ but forms a precipitate of HgS when warmed.

Acid solutions of As and Sb yield precipitates with a hot solution of $S_2O_3^{--}$, the product being As_2S_3 and Sb_2S_3 respectively (distinction from Sn which is not precipitated). Solutions of Cu^{++} on long standing with $S_2O_3^{--}$ form $Cu_2S_2O_3$ which is changed by boiling to Cu_2S and H_2SO_4[2] (separation from Cd):

$$2\ Cu(NO_3)_2 + 3\ Na_2S_2O_3 = Cu_2S_2O_3 + Na_2S_4O_6 + 4\ NaNO_3$$

$$Cu_2S_2O_3 + H_2O = Cu_2S + H_2SO_4$$

Solutions of Fe^{+3} are reduced to Fe^{++} by $S_2O_3^{--}$: $2\ FeCl_3 + 2\ Na_2S_2O_3 = 2\ FeCl_2 + 2\ NaCl + Na_2S_4O_6$.[3] Metallic Al in alkaline solution quickly reduces $S_2O_3^{--}$ to S^{--}.[4] Zinc and HCl will accomplish the same result. Dichromates are reduced to Cr^{+3} by $S_2O_3^{--}$. Permanganates, in neutral solution, become MnO_2; in acid solution the reduction is to Mn^{++}, a sulfate and dithionate being formed. Mn^{++} and Zn^{++} give no precipitate with $S_2O_3^{--}$ (distinction from S^{--}).

Barium chloride forms, with $S_2O_3^{--}$, a white precipitate of barium thiosulfate, BaS_2O_3, slightly soluble in H_2O. The corresponding strontium salt is formed only from a fairly concentrated solution while the calcium salt is readily soluble in H_2O (distinction from SO_3^{--}).

B. **With non-metals and their compounds.** — When $S_2O_3^{--}$ is treated with an acid the main reaction is $H_2S_2O_3 = H_2SO_3 + S$. In addition, side reactions also take place:

$$2\ H_2S_2O_3 = H_2S + H_2S_3O_6$$

$$2\ H_2S_2O_3 = H_2S_4O_5 + H_2O\ [5]$$

These reactions are promoted by weak acids (CO_2 or H_3BO_3) as well as strong, although the latter act more quickly. In slightly alkaline solution $Na_2S_2O_3$ is decomposed on boiling: $2\ Na_2S_2O_3 = Na_2S + Na_2S_3O_6$. With NaCN a solution of $S_2O_3^{--}$ forms the corresponding thiocyanate: $Na_2S_2O_3 + NaCN = Na_2SO_3 + NaCNS$.

Thiosulfates are reducing agents — even stronger and more active than the sulfites to which they are so easily converted. This reduction is

[1] Cf. Sander, *Z. angew. Ch.*, **31**, 197 (1918), *C.A.* **13**, 937.

[2] Cf. Bassett and Durrant, *J. Ch. Soc.*, **123**, 1279 (1923); cf. Hanus and Hovorka (*C.A.* **23**, 4418).

[3] This reaction forms the basis for a volumetric method for $S_2O_3^{--}$, a solution of CNS^- being used as an indicator.

[4] de Koninck, *Z. anal. Ch.*, **26**, 26 (1887).

[5] Bassett and Durrant, *J. Ch. Soc.*, **1927**, 1416. Cf. von Deines, *Z. anorg. allgem. Ch.*, **177**, 13 (1928), *C.A.* **23**, 1834; Riesenfeld and Sydow, *Ibid.*, **175**, 49 (1928), *C.A.* **23**, 352.

illustrated by the action on arsenic compounds, on Fe^{+3}, $Cr_2O_7^{--}$ and MnO_4^- as given above. The $S_2O_3^{--}$ forms a sulfate or acid-sulfate ion, depending upon conditions. Hydrogen peroxide in acetic acid solution readily oxidizes $S_2O_3^{--}$ to $S_4O_6^{--}$:

$$2\,Na_2S_2O_3 + H_2O_2 + 2\,HC_2H_3O_2 = Na_2S_4O_6 + 2\,NaC_2H_3O_2 + 2\,H_2O$$

In alkaline solution, however, the reaction between $S_2O_3^{--}$ and Na_2O_2 results in the formation of SO_4^{--}.

Thiosulfates may be titrated with I_2 in an acetic acid solution: $2\,Na_2S_2O_3 + I_2 = 2\,NaI + Na_2S_4O_6$. In alkaline solution the main product is said to be Na_2SO_4.[1] Chlorine and bromine react more vigorously than iodine. An excess of either forms SO_4^{--} from $S_2O_3^{--}$:

$$Na_2S_2O_3 + 4\,Cl_2 + 5\,H_2O = 2\,NaHSO_4 + 8\,HCl$$

The same is true of ClO^-, BrO^- and IO^-, although under some conditions, especially in a dilute solution, the reaction is more complicated: $3\,Na_2S_2O_3 + 5\,NaClO = 2\,Na_2SO_4 + Na_2S_4O_6 + 5\,NaCl$. Chloric, bromic and iodic acids are first reduced to the corresponding halogens and then, with an excess of $S_2O_3^{--}$, to the halides, always accompanied by the separation of S°. Nitric acid is reduced to NO with the liberation of S°.

7. Ignition. — All thiosulfates are decomposed upon ignition. Those of the alkali metals form sulfates and polysulfides (Eq. 1), others yield sulfurous acid and a sulfide or sulfate or both. The capacity of thiosulfates for rapid oxidation renders their mixture with chlorates, nitrates, etc., *explosive*. Cyanides and ferricyanides, fused with thiosulfates, form thiocyanates which may be extracted from the melt by alcohol. When fused on charcoal with Na_2CO_3, thiosulfates form sulfides (Eq. 2, 3). Other reducing agents in place of the charcoal will effect the same result. Fusion with an alkali carbonate and nitrate or chlorate results in the formation of a sulfate (Eq. 4). Ignition of a metallic salt with $Na_2S_2O_3$ in a dry test tube gives the sulfide of the metal. In the case of As, Sb or Sn a thio-salt is formed, hence $Na_2S_2O_3$ may be substituted for $Na_2CO_3 + S$ in the preparation of these compounds.[2]

$$(1)\quad 4\,Na_2S_2O_3 = Na_2S_5 + 3\,Na_2SO_4$$
$$4\,Na_2S_2O_3 = 3\,Na_2SO_4 + Na_2S + 4\,S$$
$$2\,Na_2S_2O_3 + 3\,O_2\text{ (air)} = 2\,Na_2SO_4 + 2\,SO_2$$
$$(2)\quad Na_2S_2O_3 + Na_2CO_3 + 2\,C = 2\,Na_2S + 3\,CO_2$$
$$(3)\quad 2\,PbS_2O_3 + 4\,Na_2CO_3 + 5\,C = 4\,Na_2S + 2\,Pb + 9\,CO_2$$
$$(4)\quad 3\,Na_2S_2O_3 + 3\,Na_2CO_3 + 4\,KClO_3 = 6\,Na_2SO_4 + 4\,KCl + 3\,CO_2$$

8. Detection. — Thiosulfate ion is distinguished (*a*) by the formation of a precipitate of S° and the evolution of SO_2 when treated with an acid; (*b*) by its action as a reductant; (*c*) by its non-precipitation of Ca^{++}. The

[1] Abel, *Z. anorg. allgem. Ch.*, **74**, 395 (1912), *C.A.* **6**, 1720.

[2] Donath, *Ch. Ztg.*, **54**, 78 (1930), *C.A.* **24**, 1594.

precipitation of sulfur with evolution of SO_2 upon addition of dilute acids is characteristic of $S_2O_3^{--}$. It will be understood, however, that in the presence of oxidizing agents, which can be brought into action by the acid, S^{--} will likewise give a precipitate of sulfur. The test for $S_2O_3^{--}$ is not obtained in less than five minutes, when using 100 cc. of a cold solution containing 1 mg. of $S_2O_3^{--}$ per cubic centimeter.[1]

If Ag^+ is added to $S_2O_3^{--}$ a precipitate is obtained which is first white, then yellow, brown, and finally black. The color changes are accelerated by heat. The white precipitate is $Ag_2S_2O_3$ which is ultimately converted to Ag_2S: $Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4$.[2]

When iodine and sodium azide are mixed no action takes place. If a small amount of $S_2O_3^{--}$ is added nitrogen will be liberated. Of the various sulfur compounds only sulfides and thiocyanates interfere.[3]

A solution of Ru_2Cl_3 made slightly alkaline with NH_4OH will turn deep red upon boiling after the addition of $S_2O_3^{--}$. The test will readily reveal one part of $S_2O_3^{--}$ in 4000 of solution.[4]

9. **Determination.** — *Gravimetrically,* thiosulfates may be determined by oxidation to sulfate which after precipitation as $BaSO_4$ is dried and weighed. *Volumetrically,* $S_2O_3^{--}$ may be oxidized to tetrathionate by standardized iodine and the excess of that reagent determined with a known solution of thiosulfate. Another method involves the addition of excess Ag^+ to the $S_2O_3^{--}$ and titration of the excess with CNS^-.[5]

§241. The Thionic Acids.

The thionic acids have the general formula $H_2S_nO_6$ where n may vary from 2 to 5.[6] Structurally their configuration may be as indicated in Table 43. One of the principal objections to the chain arrangement is that it does not explain the limitation to the number of sulfur atoms. Moreover, certain reactions are not easily accounted for by the formulas given. Other suggested groupings, however, are equally unsatisfactory in some respect.[7]

None of the thionic acids have been isolated in the pure state. Their aqueous solutions are readily obtained by the action of acids on the thiosulfate ion or of H_2S on H_2SO_3 (see below) but cannot be concentrated sufficiently to cause separation of the free acid. When evaporated, even at room temperature, such solutions undergo decomposition.

[1] Hackl, *Ch. Ztg.*, **47**, 174 (1923), *C.A.* **17**, 1930.

[2] Cf. Hackl, *loc. cit.*, p. 210, 466.

[3] Jelley and Clark, *Brit. J. Phot.*, **76**, 714–6 (1929), *C.A.* **24**, 3967, place one drop of the unknown in a small crucible, add one drop of starch iodide and then one drop of 2% NaN_3. If the liquid contains more than 0.0_51 N $S_2O_3^{--}$ the blue color disappears.

[4] For other tests, see: Gutzeit, *Helv. Ch. Acta*, **12**, 713 (1929), *C.A.* **23**, 4645. For the detection of $S_2O_3^{--}$ when other sulfur acids are present, see: Rüdisüle, VII, 1, p. 665–72.

[5] Cf. Rüdisüle, VII, 1, p. 673–700.

[6] The potassium salt of hexathionic acid, $K_2S_6O_6$, has been reported. It is said to be stable when dry but quickly decomposed in solution. Partington and Tipler, *J. Ch. Soc.*, **1929**, 1382.

[7] For a discussion of this subject see: Bassett and Durrant, *J. Ch. Soc.*, **1927**, 1401–68; Christiansen, *Z. Elektroch.*, **34**, 638–40 (1928); Vogel, *J. Ch. Soc.*, **127**, 2248–9 (1925).

The products are usually SO_4^{--}, SO_2 and S°. In general, $H_2S_4O_6$ is the most stable acid, $H_2S_3O_6$ the least, while $H_2S_5O_6$ is intermediate.[1] The solid salts decompose, when heated, to form similar products, except that dithionates yield no S°.

If prepared as indicated above, trithionic acid is believed by some investigators[2] to be formed first. Subsequently the ratio of tri-, tetra- and pentathionic acid present in the system will depend upon the concentration of H^+, a small quantity favoring $H_2S_3O_6$ while a large amount tends to promote the formation of $H_2S_5O_6$.[3]

A solution of the thionic acids gives no precipitate with Ba^{++}. Treated with mercurous nitrate, $S_3O_6^{--}$ gives a black precipitate, while $S_4O_6^{--}$ and $S_5O_6^{--}$ both produce a yellow precipitate. Treated with a strong oxidant thionates are readily converted to SO_4^{--} which may be precipitated as $BaSO_4$, dried and weighed. In the presence of Zn° and HCl thionates are reduced to H_2S which may be absorbed and the amount determined by means of standardized I_2 as usual.[4]

Dithionic Acid, $H_2S_2O_6$. — This compound is known only in the form of its salts and as a solution of the acid in water. The manganous salt is prepared by the action of H_2SO_3 upon MnO_2[5] suspended in ice-cold water: $MnO_2 + 2\,H_2SO_3 = MnS_2O_6 + 2\,H_2O$. Similar results are obtained with NiO_2 or Fe_2O_3. It has been stated[6] that dithionates may be prepared in 75% yield by heating $Na_2SO_3{\cdot}7H_2O$ with PbO_2 and H_2O until all of the sulfite is in solution. After addition of CO_2, filtration, neutralization and addition of lactic acid, the resulting solution is concentrated to produce crystallization of the desired salt. The acid $H_2S_2O_6$ may be obtained by treating MnS_2O_6 with $Ba(OH)_2$ and the filtrate from this reaction with CO_2 or the calculated amount of H_2SO_4. A colorless solution is obtained, which may be evaporated in a vacuum until it has a specific gravity of 1.347. It decomposes upon further heating: $H_2S_2O_6 = H_2SO_4 + SO_2$. (All other thionic compounds decompose upon heating with separation of sulfur.) Upon exposure to air $H_2S_2O_6$ is oxidized to H_2SO_4. A cold solution of $S_2O_6^{--}$ is not affected by ClO^-, BrO^- or MnO_4^- but Na_2O_2 oxidizes it to SO_4^{--}. All dithionates are soluble in water; the least soluble is $K_2S_2O_6$ — 6.23 g./100 cc. of H_2O. Salts[7] of the alkali and alkaline earth metals are the most stable. Their aqueous solutions may be heated to the boiling point without decomposition.[8]

Trithionic Acid, $H_2S_3O_6$. — The free acid is not known. The potassium salt may be obtained by treating $K_2S_2O_3$ with sulfur dioxide: $2\,K_2S_2O_3 + 3\,SO_2 = 2\,K_2S_3O_6 + S°$. Another method involves the reaction: $K_2S + 4\,KHSO_3 + 4\,SO_2 = 3\,K_2S_3O_6 + 2\,H_2O$. If a solution of $KHSO_3$ is allowed to stand for any length of time, $S_3O_6^{--}$ is formed. When a slightly alkaline solution of $Na_2S_2O_3$ is warmed with Na_2PbO_2 the products $Na_2S_3O_6$ and PbS are obtained. Sodium thiosulfate may also be converted to the trithionate by oxidation with H_2O_2 in an ice-cold solution: $3\,Na_2S_2O_3 + 4\,H_2O_2 = 2\,Na_2S_3O_6 + 3\,H_2O + 2\,NaOH$. As indicated above, the first thionic acid to be formed when $S_2O_3^{--}$ is treated with H^+ is $H_2S_3O_6$. The amount of tetra- and penta- acids produced is dependent upon the $[H^+]$. An interesting method for the preparation of trithionates involves the heating of a silver or mercurous double thiosulfate: $2\,NaAgS_2O_3 +$ heat $= Na_2S_3O_6 + Ag_2S$. The acid $H_2S_3O_6$ may be obtained by adding perchloric or fluosilicic acid to a solution of $K_2S_3O_6$.

Trithionic acid is the least stable of the group. Its aqueous solutions slowly decom-

[1] Foerster and Hornig, *Z. anorg. allgem. Ch.*, **125**, 86 (1923), *C.A.* **17**, 1394.

[2] See: Bassett and Durrant, *loc. cit.*

[3] Cf. Kurtenacker and Czernotzky, *Z. anorg. allgem. Ch.*, **175**, 367–82 (1928), *C.A.* **23**, 1340; Foerster, *Ibid.*, **139**, 246–60 (1924), *C.A.* **19**, 790; Riesenfeld and Feld, *Ibid.*, **119**, 225–70 (1921), *C.A.* **16**, 1714.

[4] Cf. Riesenfeld and Sydow, *Z. anorg. allgem. Ch.*, **175**, 74 (1928), *C.A.* **23**, 60; Kurtenacker, *et al.*, *Ibid.*, **166**, 178 (1927), *C.A.* **22**, 362; *Ibid.*, **121**, 335 (1922), *C.A.* **16**, 2921; Rüdisüle, VII, 1, p. 710.

[5] Cf. De Baat, *Rec. trav. ch.*, **45**, 237 (1926), *C.A.* **20**, 2293.

[6] Hac (*C.A.* **23**, 3869).

[7] Only normal salts are known.

[8] Fischer and Classen, *Z. angew. Ch.*, **35**, 198 (1922), *C.A.* **16**, 2278, have suggested a method for the volumetric determination of $H_2S_2O_6$ based on its greater stability when compared with the other sulfur acids.

pose at room temperatures: $H_2S_3O_6 = H_2SO_4 + SO_2 + S°$. In strongly alkaline solution the products are SO_3^{--} and $S_2O_3^{--}$, no sulfate being formed: $2 H_2S_3O_6 + 3 H_2O = H_2S_2O_3 + 4 H_2SO_3$. In strongly acid solution over one-third of the original sulfur is converted to SO_4^{--}; some H_2S is also formed. The hydrolysis of $S_3O_6^{--}$ is accelerated by Cu^{++}, Ag^+ and Hg^{++}, the corresponding sulfide being precipitated. Although the salts of $H_2S_3O_6$ are comparatively stable, in solution they gradually decompose. The presence of H^+ hastens the decomposition.[1] Many of the trithionates are readily soluble in water, the Hg_2^{++}, Hg^{++} and Ag^+ compounds are only slightly soluble. The alkali salts, however, are the only ones that are even fairly well known. If a solution of $S_3O_6^{--}$ is treated with Ag^+ a white precipitate is first formed which gradually turns black; $HgCl_2$ in excess forms the white complex $HgCl_2 \cdot 2HgS$; $CuSO_4$ ultimately forms CuS. The salts of $H_2S_3O_6$ are not oxidized by ClO_3^- or IO_3^-, but an acid solution is rapidly changed to SO_4^{--}, some S° also being formed. Iodine apparently oxidizes $S_3O_6^{--}$ to SO_4^{--}. If a trithionate is treated with $CuCl_2$, $BaCl_2$ and HCl, then boiled for one hour, all of the sulfur is precipitated as $BaSO_4$. This test is said to be satisfactory in the presence of sulfite, thiosulfate and tetrathionate.[2]

Tetrathionic Acid, $H_2S_4O_6$. — Pure tetrathionic acid, $H_2S_4O_6$, has not been isolated in spite of the fact that it is the most stable of the thionic acids. Its dilute solution may be boiled without decomposition. A concentrated solution decomposes into H_2SO_4, SO_2 and S°. In acid properties it is as strong as $H_2S_2O_6$.

Tetrathionates are readily prepared by adding iodine to thiosulfates: $2 Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2 NaI$. A number of the other oxidants will effect the same result: PbO_2, Fe^{+3}, Cu^{++}, MnO_4^-, BaO_2, SeO_2, Cl_2, Br_2, H_2O_2, etc.: $2 Na_2S_2O_3 + O + H_2O = Na_2S_4O_6 + 2 NaOH$. An essential factor is the neutralization of the base as it is formed. If $Na_2S_2O_3$ is treated with SO_2 tetrathionate is produced along with small amounts of $S_3O_6^{--}$ and $S_5O_6^{--}$. Traces of arsenite favor formation of the $S_4O_6^{--}$.[3]

The salts of $H_2S_4O_6$ are generally soluble in H_2O. In the solid state they may be kept for a month or more, but they readily decompose in solution, especially when warmed. The alkali salts are more stable than those of Ba^{++}, Cu^{++}, etc.

Tetrathionic acid in cold solution is not affected by non-oxidizing mineral acids. Strong oxidants convert the $S_4O_6^{--}$ to SO_4^{--}; strong reducing agents form $S_2O_3^{--}$ and ultimately S^{--}. The course of the reaction in either case is obviously dependent upon conditions. If $S_4O_6^{--}$ is treated with an alkali, $S_2O_3^{--}$ and $S_3O_6^{--}$ are formed: $4 Na_2S_4O_6 + 6 NaOH = 5 Na_2S_2O_3 + 2 Na_2S_3O_6 + 3 H_2O$. If the system is hot some S^{--} is obtained.[4] The addition of an alkali carbonate to $S_4O_6^{--}$ results in the formation of some sulfate: $2 Na_2S_4O_6 + 2 Na_2CO_3 = 3 Na_2S_2O_3 + Na_2S_3O_6 + Na_2SO_4 + 2 CO_2$.[5] An excess of $HgCl_2$ added to $S_4O_6^{--}$ gives the white $HgCl_2 \cdot 2HgS$. Stannous chloride also produces a white precipitate. Hydroxylamine in acid solution acts according to the equation: $H_2S_4O_6 + NH_2OH + H_2O = 2 H_2SO_4 + 2 S + NH_3$. In alkaline solution the reaction is: $Na_2S_4O_6 + 2 NH_2OH + 3 NaOH = 2 Na_2S_2O_3 + NaNO_2 + NH_3 + 3 H_2O$.[6]

Tetrathionates differ from pentathionates in that with the former (*a*) no precipitate of S° is obtained upon addition of KOH; (*b*) no decomposition takes place when an ammoniacal solution is treated with H_2S; (*c*) $Ag(NH_3)_2^+$ gives no precipitate.

Pentathionic Acid, $H_2S_5O_6$. — This acid has not been isolated; its aqueous solution and its salts are the only forms known. In a cold solution it may be kept for a few months, but even under the most favorable conditions it slowly decomposes to give S° and other sulfur acids — $H_2S_4O_6$, $H_2S_3O_6$, etc. If a solution of $H_2S_5O_6$ is heated rapid decomposition takes place with formation of H_2SO_4, SO_2, S° and a small amount of H_2S. In strongly acid solution $H_2S_5O_6$ is the most stable of the thionic acids.

Pentathionic acid may be prepared by treating a cold solution of $Na_2S_2O_3$ with an

[1] Cf. Hornig, *Z. anorg. allgem. Ch.*, **176**, 423 (1928), *C.A.* **23**, 1075.

[2] Riesenfeld and Sydow, *loc. cit.*

[3] Cf. Sander, *Z. angew. Ch.*, **28**, I, 273 (1915), *C.A.* **9**, 2357; Colefax, *J. Ch. Soc.*, **93**, 798 (1908).

[4] Cf. Gutmann, *Ber.*, **40**, 3614 (1907), *C.A.* **2**, 381.

[5] *Ibid.*, **41**, 300 (1908), *C.A.* **2**, 1246.

[6] *Ibid.*, **53**, 444 (1920), *C.A.* **14**, 1944.

arsenite and HCl. The system may be concentrated at 35° and filtered. The filtrate will contain about 60% of $H_2S_5O_6$, free from $S_3O_6^{--}$ or $S_4O_6^{--}$. Another method involves the addition of H_2S to a solution of SO_2 at 0°, followed by filtration. The filtrate is known as Wackenroder's solution. In addition to $H_2S_5O_6$ it contains some of the tri- and tetra-acids.[1]

The salts of pentathionic acid are all unstable. In either the solid state or in solution they readily decompose to give S°: $K_2S_5O_6 = K_2SO_4 + 3\ S$. A small amount of H_2SO_4 or HCl retards the decomposition but does not completely arrest it. The salts are all readily soluble in water. In solution they are easily decomposed by bases, the separation of S° on addition of an alkali being almost as delicate a test for $S_5O_6^{--}$ as is $Ag(NH_3)_2^+$ (see below). A solution of Sn^{++} gives a dark brown precipitate with $S_5O_6^{--}$; ammoniacal mercuric cyanide forms HgS. If H_2S is added to a solution of $H_2S_5O_6$, complete decomposition takes place: $H_2S_5O_6 + 5\ H_2S = 10\ S + 6\ H_2O$. Potassium chlorate in the presence of HCl completely oxidizes $S_5O_6^{--}$ to SO_4^{--}.

The detection of $S_5O_6^{--}$ is effected by noting its reaction with $Ag(NH_3)_2^+$. At first a faint brown color appears, which darkens as the quantity of precipitate increases. Sulfites interfere.[2]

§242. Sulfurous Acid. H_2SO_3

1. Physical Properties. — Sulfurous acid, so called, is largely an aqueous solution of sulfur dioxide, SO_2, only a small portion actually combining with the water to form H_2SO_3.[3] The dioxide is a colorless gas, having a strong, suffocating odor; critical temperature, 157.50° ± 0.05°; critical pressure, 77.79 ± 0.05 atmospheres;[4] boiling point of the liquid, −10.02° ± 0.1° at 760 mm.;[5] weight of one liter at 15° and 760 mm., 2.9266 g. In an open dish liquid SO_2 evaporates rapidly, the temperature of the remaining liquid dropping to −75°. Evaporation under diminished pressure yields a woolly solid. If quickly cooled to −76° a snow-white solid is obtained. The dry gas is not combustible in air and does not react acid to litmus. In the presence of moisture it has a distinct acid reaction. The gas and its aqueous solution are poisonous, due to absorption by the blood in which oxidation to H_2SO_4 takes place. As little as $0.0_35\%$ can be detected by the odor; 0.05% is intolerable. Vegetation is injured if the air contains more than 0.003% of the gas. Normal sulfites are not appreciably toxic.

Sulfur dioxide is readily soluble in water where it apparently exists chiefly as SO_2 molecules, a small amount of the hexahydrate, $SO_2 \cdot 6H_2O$, and a very small quantity of H_2SO_3 being formed. The pure acid, H_2SO_3, has not been isolated, but its acid and normal salts are readily obtained. It has a strong odor due to the escaping SO_2 which may be more quickly expelled by boiling. The acid oxidizes slowly in the air, forming H_2SO_4, hence sulfurous acid usually gives a test for SO_4^{--}.[6] The structure of H_2SO_3 has not been definitely established; the dioxide is believed to be $S\begin{smallmatrix}\diagup O \\ | \\ \diagdown O\end{smallmatrix}$ rather than $O{=}S{=}O$.[7]

Moist SO_2 or a solution of the gas is a strong bleaching agent. Wool, silk, feathers, sponge, etc., are permanently affected; the same is true of many vegetable substances, as straw, wood, etc.; yellow colors and chlorophyll are not bleached; red roses are only temporarily changed. Other uses for SO_2 are (*a*) as a preservative for dried fruits, etc.;

[1] Cf. Friend, VII, 1, p. 220, *et seq.*; Josephy, *Z. anorg. allgem. Ch.*, **135**, 21 (1924), *C.A.* **18**, 3331, has also studied the preparation of pentathionic acid.

[2] Czernotzky, *Z. anorg. allgem. Ch.*, **175**, 402 (1928), *C.A.* **23**, 60. For other tests see: Rüdisüle, VII, 1, p. 711–726.

[3] Dietzel and Galanos, *Z. Elektroch.*, **31**, 466 (1925).

[4] Cardoso and Fiorentino, *J. ch. phys.*, **23**, 841 (1926).

[5] Bergstrom, *J. Phys. Ch.*, **26**, 876 (1922).

[6] Light seems to play an important part in this oxidation.

[7] Rankine and Smith, *Proc. Phys. Soc. (London)*, **35**, 33 (1922).

(*b*) as a disinfectant; (*c*) for refrigerating purposes; (*d*) to assist in converting wood into paper pulp; (*e*) for conversion into SO_3 to make sulfuric acid.

2. Occurrence. — Sulfur dioxide is found in volcanic gases and in the spring waters of volcanic regions. It can also be detected in the air of manufacturing communities where large quantities of coal are used for fuel.

3. Preparation. — (*a*) Sulfur burns in air at about 250° to form SO_2. The product may contain 2%–7% SO_3 and of course the nitrogen which is unaffected. (*b*) Sulfur dioxide may be obtained by roasting various sulfides: $4\ FeS_2 + 11\ O_2 = 2\ Fe_2O_3 + 8\ SO_2$. The "flue gases" containing 6%–7% SO_2 are allowed to pass upward through an "absorber." Water, trickling down over the packing in the absorber, takes up the SO_2 to form a 1% solution. This is heated to expel the SO_2 which is liquefied and stored in cylinders.[1] (*c*) An interesting method advocated by Moliter[2] involves heating to 800° a mixture of anhydrite ($CaSO_4$), coke, powdered shale and clay. The products are cement and an exit gas containing 6%–7% SO_2 which may be recovered as in (*b*) above. (*d*) Concentrated H_2SO_4 may be heated with various metals as Cu, Ag, Hg and Zn to give SO_2. Between 130° and 170° the reaction with Cu° is said to be:

$$6\ Cu + 6\ H_2SO_4 = 4\ CuSO_4 + Cu_2S + SO_2 + 6\ H_2O$$ [3]

Carbon and sulfur also cause decomposition:

$$C^\circ + 2\ H_2SO_4 = CO_2 + 2\ SO_2 + 2\ H_2O$$
$$S^\circ + 2\ H_2SO_4 = 3\ SO_2 + 2\ H_2O$$

(*e*) Heating the sulfate of an alkaline earth metal with Fe° or C° results in the formation of SO_2: $CaSO_4$ at 750° gives CaS and SO_2; $SrSO_4$ and $BaSO_4$ decompose at 850° and 950° respectively. At 900° the reaction with $CaSO_4$ is rapid and the yield of SO_2 about 80% of theory. If gypsum and blast furnace slag are heated to 1400° a good yield of SO_2 is obtained.[4] (*f*) A convenient laboratory method for the preparation of SO_2 in a Kipp generator is based upon the decomposition with dilute H_2SO_4 of cubes composed of three parts calcium sulfite and one part calcium sulfate.

Preparation of sulfites. — Sulfites of the common metals are usually made by the action of sulfurous acid upon the oxides or hydroxides of the metals. They are normal, except mercurous, which is acid, and chromium, aluminum and copper, which are basic. Sulfurous acid precipitates from solution ions of Groups I and II except Cu^{++} and Cd^{++}.

Sulfites of the alkalis precipitate from solution ions of the other metals except Cr^{+3}. The sulfites of Ag, Hg, Cu and Fe^{+3} are unstable, the SO_3^{--} becoming SO_4^{--} at the expense of the base. With the unstable stannous sulfite the action is the reverse. All sulfites upon exposure to air slowly absorb oxygen, and are partially converted into sulfates. *Bisulfites* are prepared by saturating cold sulfite solutions with SO_2. The solid salt may in many cases be isolated by adding sufficient alcohol. Metabisulfites are formed by the union of two molecules of a bisulfite with the elimination of H_2O: $2\ M^+HSO_3 = H_2O + M_2S_2O_5$.

5. Solubilities. — Sulfur dioxide is readily soluble in water with evolution of heat. At 20° the solubility is 10.64 g./100 g. of water.[5] Acetic acid dissolves more than 300 volumes of SO_2 at 0° and 760 mm. The minimum solubility in H_2SO_4 is reached at a concentration of 85.8% in which 2.80 g. of SO_2 will dissolve in 100 g. of the solvent. The solubility increases with either a decrease or an increase in strength of the H_2SO_4.[6]

[1] It has been stated that if the SO_2 thrown away annually in the United States by smelters of sulfide ores were converted into H_2SO_4 there would be no need to use sulfur for that purpose.

[2] Moliter, *Ch. Ztg.*, **51**, 329, 370 (1927).

[3] Druce, *Ch. News*, **136**, 81 (1928).

[4] Neumann, *Z. angew. Ch.*, **39**, 1537 (1926).

[5] Hudson, *J. Ch. Soc.*, **127**, 1332 (1925).

[6] Cf. Friend, VII, 2, p. 110–1.

The sulfites of the alkali metals are readily soluble in water; the normal sulfites of all other metals are insoluble to slightly soluble. The sulfites of the alkaline earth metals, and some others, are soluble in a solution of SO_2 but are reprecipitated upon boiling. The alkalis form acid sulfites (bisulfites), which can be obtained in the solid state by precipitation from a solution containing excess SO_2. Evaporation of such a system yields metabisulfites, $M_2S_2O_5$.[1] The sulfites are insoluble in alcohol. They are decomposed by all acids except carbonic, boric and, in some instances, hydrosulfic.

Aqueous solutions of SO_2 slowly decompose at room temperature forming ultimately H_2SO_4 and S°.[2] In the absence of air the reaction is believed to be: $3\ H_2SO_3 = 2\ H_2SO_4 + S^\circ + H_2O$.[3] Decomposition is inhibited by the presence of a strong acid, as $2\ N$ HCl; accelerated by $CoSO_4$.[4] Solutions of bisulfites undergo decomposition more rapidly than do those of sulfites.[5]

6. Reactions. — *A*. **With metals and their compounds.** — Sulfurous acid forms three classes of salts: *normal*, as sodium sulfite, Na_2SO_3; *acid*, as sodium bisulfite, $NaHSO_3$; and *meta*, as sodium metabisulfite, $Na_2S_2O_5$. It reacts with Zn, Fe, Sn and Cu to form hyposulfurous acid, $H_2S_2O_4$.[6] Zn° in the presence of HCl reduces H_2SO_3 to H_2S:

$$3\ Zn + 6\ HCl + H_2SO_3 = 3\ ZnCl_2 + H_2S + 3\ H_2O$$

Sulfurous acid precipitates simple, positive ions of first and second group metals except those of Cu^{++} and Cd^{++}; ions of other metals are not precipitated owing to the solubility of the sulfites in acids.

Alkali sulfites precipitate the positive ions of all other metals. The compounds, mostly white, are soluble in acetic acid. Any excess of the reagent tends to combine with the metal sulfites to form soluble complexes in which various properties of the metal ion are obscured. The precipitates of Pb, Hg, Ba, Sr and Ca are usually accompanied by sulfates, due to the fact that solutions of SO_3^{--} nearly always contain SO_4^{--}.

A solution of lead acetate precipitates SO_3^{--} as $PbSO_3$, white, easily soluble in dilute HNO_3, and not blackening when boiled (distinction from thiosulfate). Ag^+ gives a white precipitate of silver sulfite, Ag_2SO_3, easily soluble in dilute HNO_3 or in excess of the reagent. The precipitate turns brown when boiled. Hg_2^{++} in dilute acid solution gives a gray precipitate of Hg°, if the acidity is above $2\ N$ oxidation to Hg^{++} takes place:[7]

[1] Cf. Getman, *J. Phys. Ch.*, **30**, 266 (1926).
[2] Cf. Reinders and Vles, *Rec. trav. ch.*, **44**, 249 (1925).
[3] See, however, Bassett and Durrant, *J. Ch. Soc.*, **1927**, 1412.
[4] Milbauer and Pazourek, *Ch. Listy*, **15**, 34 (1921), *C.A.* **15**, 1666.
[5] For a discussion of the auto-decomposition of bisulfites see: Foerster and Haufe, *Z. anorg. allgem. Ch.*, **177**, 17–41 (1929), *C.A.* **23**, 2383.
[6] Schützenberger, *Compt. rend.*, **69**, 196 (1869).
[7] Stewart and Wardlaw, *J. Ch. Soc.*, **121**, 1481–9 (1922).

$2\ Hg_2Cl_2 + 4\ HCl + SO_2 = 4\ HgCl_2 + 2\ H_2O + S$. A solution of $HgCl_2$ produces no change in the cold, but on boiling the white Hg_2Cl_2 is precipitated with formation of H_2SO_4: $2\ HgCl_2 + 2\ H_2O + SO_2 = Hg_2Cl_2 + 2\ HCl + H_2SO_4$. Further digestion produces Hg°. These changes are, however, dependent upon the acidity of the system as indicated above. The action of Cu_2^{++} and Cu^{++} on SO_3^{--} is similar to that of the ions of mercury; in dilute acid solution Cu^{++} is reduced to Cu_2^{++}, in concentrated acid Cu_2^{++} is oxidized to Cu^{++}. Ions of Au are precipitated from solution as Au° by H_2SO_3. Stannous tin reacts with SO_2 to form first SnS, then yellow SnS_2. If the concentration of H^+ is high the Sn^{++} is oxidized directly to Sn^{+4}: $3\ SnCl_2 + 6\ HCl + SO_2 = 3\ SnCl_4 + H_2S + 2\ H_2O$.[1] Ferrous and ferric iron also react with SO_2, the former being oxidized and the latter reduced in concentrated and dilute acid respectively.[2] A solution of Ba^{++} gives a white precipitate of barium sulfite, $BaSO_3$, easily soluble in dilute HCl (distinction from $BaSO_4$). Addition of an oxidizing agent to the HCl solution results in the precipitation of $BaSO_4$. Calcium reacts similar to barium, the precipitate of $CaSO_3$ being less soluble in water than $CaSO_4$.

Sulfurous acid and sulfites are active reducing agents by virtue of their capacity for oxidation to sulfuric acid and sulfates. Some reactions illustrating this point have already been given. The following also should be noted: PbO_2 forms $PbSO_4$; AsO_4^{-3} forms AsO_3^{-3} and SO_4^{--}; Sb^{+5} becomes Sb^{+3}; $Cr_2O_7^{--}$ forms Cr^{+3}; MnO_4^- yields Mn^{++} ($2\ KMnO_4 + 5\ SO_2 + 2\ H_2O = K_2SO_4 + 2\ MnSO_4 + 2\ H_2SO_4$); MnO_2 in the cold forms manganous dithionate, $Mn_2S_2O_6$; the higher valences of Co and Ni become Co^{++} and Ni^{++}.

B. **With non-metals and their compounds.** — Sulfurous acid reacts as a reducing agent toward other acids, except hypophosphorous, phosphorous and hydrosulfic.

1. *$H_3Fe(CN)_6$* forms $H_4Fe(CN)_6$ and H_2SO_4.
2. *HNO_2* and *HNO_3* form NO and H_2SO_4, the former being reduced more readily than the latter.
3. *Hydrogen peroxide* oxidizes sulfites to sulfates.
4. *Phosphine* is oxidized to H_3PO_4. The same is true of H_3PO_2 and H_3PO_3.
5. *Hydrosulfic acid* forms only S°: $2\ H_2S + SO_2 = 3\ S + 2\ H_2O$. This reaction takes place only in the presence of moisture.
6. The free *halogens*, Cl_2, Br_2 and I_2,[3] react with SO_2 to form the cor-

[1] Durrant, *J. Ch. Soc.*, **107**, 622 (1915).

[2] Carter and James, *J. Ch. Soc.*, **125**, 2231 (1924). For an extended discussion of the action of SO_2 in solutions varying in acidity see: Wardlaw, *et al.*, *J. Ch. Soc.*, **117**, 1093, 1241 (1920); **121**, 210, 1481 (1922); **123**, 969, 3417 (1923); Carter and Butler, *Ibid.*, **123**, 2370 (1923); Foerster, *et al.*, *Z. anorg. allgem. Ch.*, **128**, 245 (1923).

[3] Cf. Macaulay, *J. Ch. Soc.*, **121**, 552 (1922).

responding halides. The halogen oxyacids, with the exception of $HClO_4$, are also reduced to the halide.

7. Nascent *hydrogen*, i.e., $Zn^\circ + H_2SO_4$, readily reduces SO_3^{--} to S^{--}: $H_2SO_3 + 6\ H = H_2S + 3\ H_2O$

7. **Ignition.** — Acid sulfites, heated in a sealed tube to 150°, are decomposed into sulfates and sulfur. Dry SO_2 is decomposed by many metals at a high temperature with formation of a sulfide and sulfate. Sulfites are decomposed by heat into oxides and SO_2: $CaSO_3 = CaO + SO_2$; but, $4\ Na_2SO_3 = 3\ Na_2SO_4 + Na_2S$. Many sulfides react, at higher temperatures, with SO_2 to form sulfates and S°. The sulfate may, of course, decompose into the oxide and SO_3.

8. **Detection.** — A solution of sulfurous acid is detected by its odor and by its decolorizing action on $KMnO_4$ or I_2. A mixture of iodic acid, HIO_3, and starch is turned violet to blue by traces of SO_3^{--}. The color is destroyed by an excess of the SO_3^{--}. Sulfites are distinguished from sulfates by failure to precipitate with $BaCl_2$ in presence of HCl. Sulfites may be converted by Zn° to hyposulfite, $S_2O_4^{--}$, which may be detected with methylene blue.[1] If zinc nitroprusside is exposed to ammonia vapors, then to SO_2, a rose-red color will appear.[2] If a 0.01% solution of Fast Blue R is added dropwise to SO_3^{--}, at first a violet, then a yellow color will appear. The test is sensitive to 1 : 175,000. Sulfide and OH^- interfere; $S_2O_3^{--}$ and polythionates do not.[3]

9. **Determination.** — *Gravimetrically*, sulfites may be oxidized to SO_4^{--}, precipitated, dried and weighed as $BaSO_4$. *Volumetrically*, SO_3^{--} may be treated with an excess of I_2[4] and the excess titrated with $Na_2S_2O_3$. This is the method usually employed. Another procedure involves titration with KIO_3 in HCl solution.[5] Sulfurous acid cannot be determined by direct titration with MnO_4^-, low results always being obtained. The addition of an excess MnO_4^- followed by back-titration is satisfactory.[6] The addition of an excess NaClO to SO_3^{--}, followed by a determination of the excess hypochlorite with KI and titration of the I_2 has also been suggested.[7, 8]

§243. Sulfuric Acid. H_2SO_4

1. **Physical Properties.** — Pure sulfuric acid is a colorless, oily liquid (oil of vitriol); density, 1.8372 at 15°; melting point, 10.5°;[9] boiling point, 270° at 755 mm., but some SO_3 is driven off to give, at 338°, a constant boiling acid which contains 98.3% H_2SO_4.

[1] Noll, *Farben-Ztg.*, **33**, 1849 (1928).
[2] Eegriwe, *Z. anal. Ch.*, **65**, 182 (1924), *C.A.* **19**, 1835.
[3] *Ibid.*, **69**, 328 (1926). Cf. Rüdisüle, VII, 1, p. 591–4.
[4] Concerning the direct titration of SO_2 with I_2 see: Maass and Maass, *J. Am. Ch. Soc.*, **50**, 1352 (1928).
[5] Ries and Clark, *Ind. Eng. Ch.*, **18**, 747 (1926).
[6] Hendrixson and Verbeck, *Ind. Eng. Ch.*, **14**, 1152–3 (1922); cf. Hendrixson, *J. Am. Ch. Soc.*, **47**, 2156 (1925).
[7] Bicskei, *Z. anorg. allgem. Ch.*, **160**, 64 (1927).
[8] For a study of some 12 methods for the determination of SO_2 see: Ries and Clark, *loc. cit.*; cf. Rüdisüle, VII, 1, p. 594 *et seq.*
[9] An excess of H_2O or of SO_3 lowers the melting point. $H_2SO_4 \cdot H_2O$ melts at 8°.

tration. The dilute or cold, concentrated acid evolves H_2; in the hot, concentrated state SO_2 is formed. The acidity and the temperature may be regulated to give an evolution of the two gases in almost any desired ratio. Secondary reactions frequently take place, thionates, sulfides and free sulfur being among the possible products.

Sulfuric acid or SO_4^{--} reacts with Ba^{++} to give barium sulfate, white, insoluble in HCl or HNO_3. This property is a distinction from all other acids except selenic and fluosilicic. The precipitate formed in the cold is finely divided and difficult to filter; if formed in a hot, acid solution and allowed to digest for a short time the separation is readily effected. In a dilute solution the mixture should stand for some time to insure complete precipitation. Solutions of Pb^{++} give a white precipitate of $PbSO_4$ not transposed by acids except H_2S, soluble in NaOH. The presence of alcohol or the absence of other acids makes the precipitation quantitative. Solutions of Ca^{++} not too dilute form a white precipitate of calcium sulfate.

Dilute H_2SO_4 does not oxidize any of the lower metallic oxides. The concentrated acid when hot effects the following changes: Hg_2O forms $HgSO_4$ and SO_2; $SnCl_2$ forms first SO_2 then H_2S which may react with the Sn^{+4} formed to precipitate SnS_2; Fe^{++} is oxidized to Fe^{+3}; all ions of manganese having a valence greater than two are reduced to Mn^{++} with the evolution of oxygen.

Some normal sulfates tend to form double salts or alums for which the general formula is $M_2^{+}SO_4 \cdot N_2^{+3}(SO_4)_3 \cdot 24H_2O$ or $M^{+}N^{+3}(SO_4)_2 \cdot 12H_2O$, e.g., $KAl(SO_4)_2 \cdot 12H_2O$, $NaCr(SO_4)_2 \cdot 12H_2O$, $NH_4Fe(SO_4)_2 \cdot 12H_2O$, etc.

B. **With non-metals and their compounds.** — When dilute H_2SO_4 transposes the salts of other acids, no other change occurs if the acid liberated is stable under the existing conditions. In ordinary reactions H_2SO_4 does not act as an oxidizing agent.

1. Many *organic compounds* are decomposed by hot, concentrated H_2SO_4, the elements of water being removed and carbon set free. Continued heating of the carbon with the hot acid results in the formation of CO_2 and SO_2: $C + 2\ H_2SO_4 = CO_2 + 2\ SO_2 + 2\ H_2O$.

Oxalic acid becomes CO_2, CO and H_2O, the H_2SO_4 remaining unchanged.

Potassium ferrocyanide with dilute H_2SO_4 forms HCN: $2\ K_4Fe(CN)_6 + 3\ H_2SO_4 = 6\ HCN + K_2FeFe(CN)_6 + 3\ K_2SO_4$.

Cyanates are decomposed into CO_2 and NH_3: $2\ KCNO + 2\ H_2SO_4 + 2\ H_2O = K_2SO_4 + (NH_4)_2SO_4 + 2\ CO_2$.

Thiocyanates are also decomposed by concentrated H_2SO_4 (p. 466).

2. *Nitrites* are decomposed with formation of nitric acid and NO: $6\ KNO_2 + 3\ H_2SO_4 = 3\ K_2SO_4 + 2\ HNO_3 + 4\ NO + 2\ H_2O$.

3. *Phosphorus* and *hypophosphites* are oxidized to H_3PO_4 with reduction of the H_2SO_4 to H_2SO_3 and then to S°.

4. *Sulfur* is slowly oxidized by hot, concentrated H_2SO_4 to H_2SO_3 with reduction of the sulfuric acid to the same compound: $2 H_2SO_4 + S = 3 SO_2 + 2 H_2O$.

Hydrosulfic acid is oxidized by H_2SO_4: $H_2S + H_2SO_4$ (concentrated) $= H_2SO_3 + S^\circ + H_2O$. Further changes may take place as indicated above.

5. *Chlorates* are decomposed when treated with concentrated H_2SO_4: $3 KClO_3 + 2 H_2SO_4 = 2 KHSO_4 + KClO_4 + 2 ClO_2 + H_2O$.

6. *Hydrobromic acid* forms Br_2 and SO_2 if the H_2SO_4 is sufficiently concentrated.

7. *Hydriodic acid* in low concentration reduces H_2SO_4 to H_2SO_3. If the amount of HI is large the reduction goes further to H_2S.[1]

7. Ignition. — Under atmospheric pressure H_2SO_4 is 50% dissociated into SO_3 and H_2O at about 625°. All sulfates fused with a fixed alkali carbonate are converted to carbonates (oxide or metal if the carbonate is decomposed at the temperature used) with formation of a fixed alkali sulfate. If a sulfate, or any other sulfur compound, is fused with Na_2CO_3 and carbon, the resulting melt will contain an alkali sulfide which, when moistened, will blacken metallic silver.

The sulfates of Cu, Sb, Fe, Hg, Bi and Al are decomposed below 650°: $2 FeSO_4 = Fe_2O_3 + SO_3 + SO_2$; $2 CuSO_4 = 2 CuO + 2 SO_3$. Below 950° the sulfates of Pb, Ag, Cd, Mn, Zn, Ni, Co and Mg are decomposed. An ordinary white heat has no effect on the sulfates of the alkalis and alkaline earth metals, but above 1200° the compounds of Ba, Sr and Ca form oxides while K_2SO_4 and Na_2SO_4 are completely volatilized, preceded by partial decomposition.[2]

Lead sulfate heated in a current of hydrogen is reduced: $2 PbSO_4 + 6 H_2 = Pb + PbS + SO_2 + 6 H_2O$. A secondary reaction takes place subsequently: $PbS + H_2 = Pb + H_2S$. Potassium acid sulfate, $KHSO_4$, heated sufficiently to eliminate H_2O forms the pyrosulfate, $K_2S_2O_7$. Further heating causes decomposition into SO_3 and the normal sulfate. The same is true of $NaHSO_4$, except that it decomposes more readily. These changes may be effected in a resistance glass container.

8. Detection. — The sulfate radical is usually detected by precipitation from hot, HCl solution as $BaSO_4$.

The sulfates insoluble in water are decomposed for analysis by long boiling with a concentrated solution of Na_2CO_3 or, more readily, by fusion with an alkali carbonate. In both cases there are produced *alkali sulfates soluble in water*, and metal *carbonates soluble in* HCl *after removing the sulfate.* $BaSO_4 + Na_2CO_3 = Na_2SO_4$ (water soluble) $+ BaCO_3$ (soluble in HCl). If the fusion mixture contains carbon, as charcoal, more or less reduction will occur, the sulfate becoming sulfide and the free metal being liberated (as with lead).

The "turpeth mineral" test for insoluble sulfates involves boiling a 10% solution of $Hg(NO_3)_2$ in 1% HNO_3 with the unknown. The formation of very small, yellow crystals of $HgSO_4 \cdot 2HgO$ indicates the presence

[1] Bush, *J. Phys. Ch.*, **33**, 613 (1929); cf. Proskouriakoff, *Ibid.*, p. 717.

[2] Concerning the thermal decomposition of some metallic sulfates see: Marchal, *J. ch. phys.*, **22**, 325 (1925), *C.A.* **19**, 3201.

of a sulfate. The action takes place in the cold with $CaSO_4$ and Hg_2SO_4, less readily with $PbSO_4$ and $SrSO_4$, and slowly with $BaSO_4$.[1]

9. Determination. — *Gravimetrically*, sulfates may be determined by precipitation as $BaSO_4$ which is dried and weighed. Small amounts of $BaSO_4$ may be determined turbidimetrically with a Parr sulfur photometer or similar device. *Volumetrically*, sulfuric acid may be titrated with a standardized alkali using methyl red as an indicator. Sulfates may be precipitated from neutral or acid solution as benzidine sulfate which may be filtered off and titrated with a standardized oxidizing agent.[2] By heating an insoluble sulfate with many times its weight of CaH_2 the sulfate is converted to sulfide which can be determined as described in §239.[3]

§244. Persulfuric Acid.[4] $H_2S_2O_8$ [5]

The anhydride, S_2O_7, was discovered by Berthelot, who obtained it by the action of a silent electric discharge upon a mixture of equal volumes of dry SO_2 and O_2. In solution the acid is obtained upon electrolysis of cold, concentrated H_2SO_4, or by the action of concentrated H_2O_2 on such a system.

At 0° persulfuric anhydride, S_2O_7, consists of flexible, crystalline needles, remaining stable for several days but gradually decomposing into SO_3 and O_2. If warmed the change takes place rapidly. The solution in water hydrolyzes in steps; first permonosulfuric acid, Caro's acid, H_2SO_5, is formed, then this is decomposed:

$$H_2S_2O_8 + H_2O = H_2SO_4 + H_2SO_5$$

$$H_2SO_5 + H_2O = H_2SO_4 + H_2O_2$$

Obviously the presence of H_2SO_4 in the solvent tends to inhibit the decomposition. The anhydride combines with SO_2 to form SO_3: $S_2O_7 + SO_2 = 3\ SO_3$.

A number of the salts of persulfuric acid have been prepared, principally by electrolysis of a cold, concentrated solution of the normal or acid sulfate, e.g., $(NH_4)_2S_2O_8$ crystallizes out when a cold solution of $(NH_4)_2SO_4$ is used;[6] $Na_2S_2O_8$ is obtained from $NaHSO_4$, etc. The salts are white, stable and moderately soluble in water,[7] $K_2S_2O_8$ apparently having the lowest solubility, 1.77 g./100 g. of H_2O at 0°.

A solution of an alkali persulfate attacks many metals,[8] forming either the ion (Cd°, Fe°, Ni°, Co°, Mg°, Zn°, etc.) or an oxide (Ag°, Pb°, Hg°, Bi°, Cu°, Mn°, etc.): $Zn^\circ + K_2S_2O_8 = ZnSO_4 + K_2SO_4$; $2\ AgNO_3 + K_2S_2O_8 + 2\ H_2O = Ag_2O_2 + 2\ KHSO_4 + 2\ HNO_3$.

Persulfates also act as powerful oxidants, changing Fe^{++} to Fe^{+3}, Cr^{+3} to Cr^{+6},[9] Ti^{+3}

[1] Deniges, *Bull. soc. ch.*, [4] **23**, 36 (1918).

[2] Knorre, *Z. anal. Ch.*, **49**, 469 (1910). Cf. Bisson and Christie, *Ind. Eng. Ch.*, **12**, 485 (1920), who have determined the solubility of benzidine sulfate in H_2O. At 25° they give 0.096 g./l.

[3] Caldwell and Krauskopf, *J. Am. Ch. Soc.*, **51**, 2936 (1929). Cf. Vilna, *Compt. rend.*, **179**, 1163 (1924), *C.A.* **19**, 791.

[4] Also called peroxydisulfuric acid.

[5] Duval and Duval, *Compt. rend.*, **191**, 843 (1931), give HSO_4.

[6] The presence of CrO_4^{--} is said to be beneficial. Cf. Mellor, X, 457.

[7] The decomposition of persulfates in H_2O has been studied by Kailan, *et al.*, *Monatsh.*, **50**, 403 (1928); *Ibid.*, **47**, 449 (1927), *C.A.* **23**, 2636, 3148. They believe that $Na_2S_2O_8$ decomposes more rapidly than $K_2S_2O_8$, and that H^+, NO_3^-, OH^- and HPO_4^{--} accelerate the reaction while K^+, Na^+ and SO_4^{--} retard it.

[8] Cf. Aschan, *Z. anorg. allgem. Ch.*, **194**, 139 (1930), *C.A.* **25**, 1454; **23**, 50.

[9] It has been stated that oxidation in alkaline solution is complete but not in acid solution unless Ag^+ is present.

to Ti^{+4} (quantitatively), Co^{++} to Co^{+3}, Ni^{++} to Ni^{+4} (in NaOH), Mn^{++} to MnO_2 (cf. p. 348), Ce^{+3} to Ce^{+4}, etc. Barium forms soluble BaS_2O_8 but if a reductant is present which reduces $S_2O_8^{--}$ to SO_4^{--} a precipitate of $BaSO_4$ will be obtained.

Ammonia is oxidized to free nitrogen by $S_2O_8^{--}$ in the presence of Ag^+:[1] $8\ NH_3 + 3\ (NH_4)_2S_2O_8(+\ Ag^+) = N_2 + 6\ (NH_4)_2SO_4$. Ammonium persulfate in the presence of Ag^+ is said to decompose according to the equation: $NH_4^+ + 4\ S_2O_8^{--} + 3\ H_2O(+\ Ag^+) \rightarrow 10\ H^+ + 8\ SO_4^{--} + NO_3^-$.[2] Potassium ferro- and ferricyanides react with $S_2O_8^{--}$ in the presence of a mineral acid to form HCN and a small amount of NH_4^+. Sodium thiosulfate, if in excess, forms a trithionate with $S_2O_8^{--}$, but if the latter is in excess a tetrathionate is obtained. The halides, Cl^-, Br^- and I^- react with $S_2O_8^{--}$ to form the elements.[3] Fe^{++} and Cu^{++} markedly accelerate the reaction, a mixture of the two being more powerful than either alone. The mechanism may be, e.g., $Fe^{++} + S_2O_8^{--} \rightarrow Fe^{+3}$; $Fe^{+3} + I^- \rightarrow Fe^{++} + I^\circ$. If Ag^+ is used as a catalyst in the presence of HNO_3, the halides are oxidized not to the free elements but to halates, $I^- \rightarrow IO_3^-$, etc.

The reaction between $S_2O_8^{--}$ and Fe^{++} or I^- or Ti^{+3} may be used for its determination. An excess of the reductant is added and the amount consumed is ascertained by back-titration with a suitable oxidant.

§245. Chlorine (Gr. *chloros* = green). Cl = 35.457. Atomic No. 17. Valence 1, 3, 4, 5 and 7. Identity first established by Davy in 1810.

1. Physical Properties. — Melting point, −101.6°; boiling point, −33.6°; critical temperature, 144°; critical pressure, 76 atmospheres. One liter of chlorine at 0° and 760 mm. weighs 3.214 g.; its density, relative to air, is 2.4494. Under ordinary conditions the molecule contains two atoms. When heated dissociation commences above 1200° and is appreciable at 1450°. Chlorine is a greenish-yellow, suffocating gas; it is not combustible in oxygen, but burns in hydrogen (sunlight promotes explosive combination).

2. Occurrence. — Chlorine is said by some authorities to occur in traces in volcanic gases. Other investigators have contradicted the statement. In combination chlorine is found in the earth's crust to the extent of about 0.055%; salt waters, e.g., the oceans and various seas, vary somewhat in Cl content, the average being about 2.07%. Vast deposits of salt, halite, NaCl, are found in various parts of the world. The Strassfurt layers in Germany are over 1200 feet thick and cover about 100 square miles; those in central New York total over 300 feet in thickness; near Detroit, Michigan, 400 feet; Petite Anse, Louisiana, over 2000 feet. Other important deposits in the United States are found in Ohio, Kansas, Virginia, California and Texas. Approximately two-thirds of the chlorine manufactured is used for bleaching, particularly pulp and paper. Large quantities are consumed in water purification, also in the manufacture of dyes, explosives and other chemicals.[4]

3. Preparation. — Practically all of the chlorine produced is made by the electrolysis of salt brine, NaCl. The gas thus obtained is liquefied and sold in cylinders or converted into bleaching powder — a mixture of $CaCl(OCl)\cdot H_2O$ and $CaO\cdot CaCl(OCl)\cdot H_2O$ in varying ratio, made by the interaction of solid calcium hydroxide and Cl_2.[5] Another commercial method that has thus far been unsuccessfully exploited involves the ignition

[1] As explained in §134 Ag_2O_2 may be the effective oxidant. Yost (see below) suggests Ag^{+3}.

[2] Marshall, *Proc. Roy. Soc. Edinburgh*, **23**, 163 (1900); Marshall and Inglis, *Ibid.*, **24**, 88 (1902). Cf. Yost, *J. Am. Ch. Soc.*, **48**, 152, 374 (1926); King, *Ibid.*, **50**, 2080 (1928).

[3] In the case of Cl^- the action may be inhibited by dilution. Iodine may be partially oxidized to iodate, IO_3^-.

[4] Cf. Kokatnur, *Ch. and Met. Eng.*, **19**, 667 (1918).

[5] Ditz, in Ullmann's Encyclopedia, 2nd ed., III, p. 332.

of $MgCl_2$ in air: $2 MgCl_2 + O_2 = 2 MgO + 2 Cl_2$. Among the older processes, almost totally abandoned now, are the Deacon and the Weldon. The former is based upon the fact that at 450° an equilibrium is attained between Cl_2, steam, HCl and oxygen, which makes possible the conversion of about two-thirds of the HCl into Cl_2. Actually, a mixture of HCl and air is passed over fire brick having a surface coating of $CuCl_2$ and heated to the temperature indicated. In the Weldon process MnO_2 reacts with HCl: $MnO_2 + 4 HCl = MnCl_2 + Cl_2 + 2 H_2O$. The manganous chloride is converted back into MnO_2 and used over again. It is claimed by some workers that $MnCl_3$ is an intermediate product in this procedure. The method, or a modification, is often used for the laboratory production of chlorine: $MnO_2 + 2 NaCl + 3 H_2SO_4 = Cl_2 + MnSO_4 + 2 NaHSO_4 + 2 H_2O$. Other procedures for obtaining small amounts of chlorine involve (*a*) dropping dilute HCl on $KMnO_4$:[1] $2 KMnO_4 + 16 HCl = 5 Cl_2 + 2 MnCl_2 + 2 KCl + 8 H_2O$; (*b*) the interaction of HCl and $KClO_3$: $KClO_3 + 6 HCl = 3 Cl_2 + KCl + 3 H_2O$; (*c*) the action of dilute H_2SO_4 on bleaching powder.

4. Oxides and Acids. — Chlorine is said to form a number of oxides, some of which need further study: Cl_2O, Cl_2O_3, ClO_2, Cl_2O_6, Cl_2O_7, ClO_4.[2] The most important acids of chlorine are hydrochloric, HCl; hypochlorous, HClO; chlorous, $HClO_2$; chloric, $HClO_3$; perchloric, $HClO_4$. These will be discussed in subsequent sections.

5. Solubility. — The solubility of chlorine in water is 1.46 g./100 cc. at 0° and normal pressure. Boiling completely removes the gas from the water.

Chlorine combines with water to form chlorine hydrate, $Cl_2{\cdot}6H_2O$,[3] which can be obtained in crystalline form by saturating a flask of water, at about 1°, with Cl_2. After a short time the crystals may be filtered off and dried between pieces of filter paper.

Chlorine slowly reacts with water to form HCl and HClO. In the sunlight the latter quickly decomposes with evolution of oxygen. The hydrolysis is favored by alkalis; opposed by the presence of H^+.

6. Reactions. — *A*. **With metals and their compounds.** — Chlorine is one of the most powerful oxidizing agents known, becoming always a chloride. All metals, in fact all elements except the noble gases, N, O and C, are attacked by moist chlorine, forming chlorides. Certain metals, e.g., Cu, Ag, Pb, Tl, form a protective coating of the chloride which materially retards further action. In some cases combination takes place with vivid incandescence. The presence of moisture is usually essential for many of the metals do not react with perfectly dry Cl_2. In the presence of acids the alteration of a metal takes place to the same degree as when that metallic compound is acted upon by HCl (§246); a chloride is formed, the metal having the same valence that would have resulted from treating the oxide or hydroxide with HCl, e.g., adding HCl to Co_2O_3 gives $CoCl_2$, hence adding Cl_2 to Co° forms $CoCl_2$, not $CoCl_3$. In alkaline mixture usually the highest degree of oxidation possible is attained. Some specific cases illustrating the action of Cl_2 are:

[1] Concerning the purity of Cl_2 made by this method see: Lewis and Wedekind, *Z. angew. Ch.*, **22**, 580 (1909), *C.A.* **4**, 31.

[2] For further discussion see: Gmelin, 8th ed., No. 6, p. 227, *et seq.*

[3] Bouzat and Azinières, *Compt. rend.*, **177**, 1444 (1923), *C.A.* **18**, 949, confirm the earlier work of Villard, *Ibid.*, **119**, 370 (1894).

1. *Pb*$^{++}$ forms PbO_2 and a chloride in alkaline mixture. With $PbCl_2$ it has been stated that $PbCl_4$ is formed.

2. *Hg*$_2^{++}$ becomes Hg^{++} in acid or alkaline solution.

3. *As*° treated with very cold Cl_2 gives $AsCl_3$. *AsO*$_3^{-3}$ is readily oxidized to AsO_4^{-3} in acid or alkaline solution.

4. *Sb*$^{+3}$ forms Sb^{+5} in acid or alkaline solution.

5. *Sn*$^{++}$ yields Sn^{+4} in acid or alkaline solution.

6. *Molybdenum* having a valence lower than six is oxidized to that condition in acid or alkaline solution.

7. *Bi*$^{+3}$ becomes Bi^{+5} in alkaline solution only.

8. *Cu*$_2^{++}$ is oxidized to Cu^{++} in acid or alkaline solution.

9. *Cr*$^{+3}$ becomes Cr^{+6} in alkaline solution only.

10. *Fe*$^{++}$ forms Fe^{+3} in acid solution. In the presence of an alkali a perferrate is obtained.

11. *Co*$^{++}$ is changed to $Co(OH)_3$ in an alkaline medium.

12. *Ni*$^{++}$ yields $NiO_2 \cdot nH_2O$ only in alkaline solution.

13. *Mn*$^{++}$ becomes MnO_2 with an alkali present.[1]

14. *Si*° heated in Cl_2 becomes $SiCl_4$.

B. **With non-metals and their compounds.**

1. *H*$_2$*C*$_2$*O*$_4$ in acid mixture: $H_2C_2O_4 + Cl_2 = 2\ CO_2 + 2\ HCl$. The $H_2C_2O_4$ must be hot and in excess. In alkaline solution the action is: $Na_2C_2O_4 + 4\ NaOH + Cl_2 = 2\ Na_2CO_3 + 2\ NaCl + 2\ H_2O$.

HCN forms cyanogen chloride, CNCl and HCl.

HCNS is changed to NH_3, H_2SO_4, CO_2 and other variable products.

H$_4$*Fe(CN)*$_6$ becomes $H_3Fe(CN)_6$. An excess of Cl_2 ultimately decomposes the ferricyanide.

2. *H*$_2$*O*$_2$ forms O_2 and HCl.

3. Chlorine does not appear to have any oxidizing action upon the oxides or acids of *nitrogen*.[2]

4. *Phosphorus*, in all valences less than five, becomes PO_4^{-3} with formation of HCl.

5. *Sulfur* in all of its lower valences is oxidized to SO_4^{--} in an acid or alkaline solution. With H_2S, sulfur is first deposited which an excess of Cl_2 changes to SO_4^{--}. A sulfide in alkaline mixture is at once oxidized to SO_4^{--} without apparent formation of the intermediate S°.

6. In alkaline solution Cl_2 oxidizes ClO^- and ClO_2^- to ClO_3^- with formation of Cl^-: $KClO_2 + Cl_2 + 2\ KOH = KClO_3 + 2\ KCl + H_2O$.

[1] For the action of Cl_2 on the sulfate and nitrate of many metals see: Schuyten, *Ch. Ztg.*, **33**, 480 (1909), *C.A.* **3**, 2420; cf. *C.A.* **2**, 931, 2518. Michael and Murphy, *Am. Ch. J.*, **44**, 365 (1910), have studied the action of Cl_2, dissolved in CCl_4, on a large number of metal oxides.

[2] Noyes and Haw, *J. Am. Ch. Soc.*, **42**, 2167, 2173 (1920), have considered the reaction between Cl_2 and NH_3.

If Cl_2 is passed into a cold solution of NaOH a hypochlorite is formed; in hot solution a chlorate is obtained:

$$2\ NaOH + Cl_2 = NaClO + NaCl + H_2O$$
$$6\ NaOH + 3\ Cl_2 = NaClO_3 + 5\ NaCl + 3\ H_2O$$

7. Chlorine does not oxidize *bromine* in acid solution; in an alkaline medium BrO_3^- and Cl^- are formed. A bromide in acid solution becomes free bromine, in alkaline mixture a bromate.

8. Iodine[1] is oxidized to HIO_3 in acid solution; in an alkaline system a periodate is formed. HI or iodides first liberate I_2 followed by further oxidation as indicated above:

$$2\ HI + Cl_2 = I_2 + 2\ HCl$$
$$I_2 + 5\ Cl_2 + 6\ H_2O = 2\ HIO_3 + 10\ HCl$$
$$KI + 4\ Cl_2 + 8\ KOH = KIO_4 + 8\ KCl + 4\ H_2O$$

A comparison of the oxidizing action of chlorine with that of bromine and iodine will reveal the fact that these elements have an oxidizing power in reverse order of their atomic weights. If all three have the same oxidizing effect, Cl_2 acts with the greatest speed. In some cases, as with cuprous copper, Cl_2 oxidizes while I_2 does not. Their hydracids are reducing agents graded in the reverse order. If any valence increase takes place in the presence of an acid due to Cl_2, Br_2 or I_2 the same increase will occur in presence of a fixed alkali. The oxidation frequently goes further in alkaline solution; thus, with Cl_2 and KOH are formed PbO_2, NiO_2, $NaBiO_3$, $Co(OH)_3$, K_2FeO_4, and MnO_2, which are not obtained in the presence of an acid.

Those oxides which are formed by Cl_2 in presence of a fixed alkali, but not of an acid, are the only ones that can be reduced by HCl. Furthermore this reduction does not always proceed to the original form; it never goes beyond that valence obtainable in presence of an acid. Thus, any Pb salt, with KOH and Cl_2, forms PbO_2. This compound, treated with HCl, again forms $PbCl_2$. Ferrous chloride with KOH and Cl_2 produces K_2FeO_4 which with HCl forms not $FeCl_2$ but $FeCl_3$, for the $FeCl_2$ can be oxidized to the tervalent state in presence of an acid.

The above is true for bromine and iodine as well as for chlorine.

8. **Detection.** — Free chlorine is recognized by its odor, its liberation of iodine from KI (starch–KI paper turns blue),[2] its bleaching action upon litmus, indigo, etc., and its action as a powerful oxidizing agent (see above).

[1] Iodine monochloride is formed by the direct action of Cl_2 on I_2. Excess of Cl_2 gives iodine trichloride, ICl_3.

[2] This test will reveal 0.03 parts of chlorine in one million parts of water. It is not specific, however.

The use of certain organic compounds for the detection of Cl_2 has also been suggested. If a solution of anilin in HCl is shaken with a small amount of Cl_2 a blue color first develops which soon changes to red. Dimethyl-*p*-phenylenediamine hydrochloride gives a bright red color in presence of Cl_2.[1] A 5% solution of *p*-aminodimethylaniline in alcohol gives a pink to red color with chlorine, iodine or bromine. The delicacy of the test increases in the order mentioned.[2]

9. Determination. — The chlorine sample may be added to a solution of potassium iodide and the liberated iodine titrated with $Na_2S_2O_3$. The chlorine may be reduced to chloride, precipitated as AgCl and weighed or titrated by Volhard's method.

§246. Hydrochloric Acid. HCl

1. Physical Properties. — The term hydrochloric acid, as commonly used, refers to a solution of the gas, hydrogen chloride, in water. This gas at S.T.P. weighs 1.63911 g./l.; when solidified it melts at − 111°, boils at − 85°; the critical temperature is 51.3°;[3] the critical pressure, 83 atmospheres.[4] It dissociates into H_2 and Cl_2 at temperatures well above 1500°.[5] Hydrogen chloride is colorless and has an acrid, irritating odor. It is readily absorbed by water. The chemically pure, concentrated solution has a specific gravity of 1.2134 and contains 43.40% HCl; the commercial product, however, has a gravity of 1.18 and averages about 36% HCl. A concentrated solution gives off gaseous HCl faster than H_2O; a dilute solution gives off H_2O faster than HCl. As a final result in either case, a constant boiling acid is obtained at 110°; it has a density of 1.10 and contains 20.24% HCl.[6] (T = 15.5° for the first two densities, 25° for the last.)

3. Preparation. — Commercially, hydrochloric acid is made (*a*) from NaCl and H_2SO_4. The HCl, expelled by heat, is absorbed in H_2O:

$$NaCl + H_2SO_4 = NaHSO_4 + HCl$$
$$NaCl + NaHSO_4 = Na_2SO_4 + HCl$$

Often only the second step in the process is utilized. Nitre cake, $NaHSO_4$, a by-product of the preparation of HNO_3, is mixed with NaCl and heated to 500°, whereupon HCl is driven off and absorbed in H_2O. (*b*) Hydrochloric acid is often obtained as a by-product of the chlorination of organic compounds. (*c*) Occasionally direct synthesis from the elements is employed: $H_2 + Cl_2 = 2\ HCl$. This procedure is applicable when, in the electrolysis of NaCl, NaOH is the product chiefly desired and there is less demand for the chlorine.[7]

Chlorides may be made by (*a*) direct union of the elements, mostly without heat. Whether an *ous* or *ic* salt is formed depends upon the amount of chlorine used. (*b*) The action of HCl upon oxides, hydroxides, carbonates or sulfites yields chlorides. The solution formed may be evaporated to expel any excess acid. If the chlorides thus formed contain water of crystallization it cannot be removed by heat alone, for some HCl will be driven off, leaving a basic salt. If the anhydrous chloride is desired, it may

[1] Alfthan (*C.A.* **23**, 53; **25**, 2071).
[2] Tremain, *Ind. Eng. Ch., Anal. Ed.*, **3**, 225 (1931).
[3] Pickering, *J. Phys. Ch.*, **28**, 123 (1924).
[4] *Ibid.*
[5] Gmelin, 8th ed., No. 6, p. 112.
[6] Bonner and Branting, *J. Am. Ch. Soc.*, **48**, 3093 (1926). Foulk and Hollingsworth, *Ibid.*, **45**, 1220 (1923). Hulett and Bonner, *Ibid.*, **31**, 390 (1909).
[7] For a number of other methods see: Gmelin, 8th ed., No. 6, p. 97–104.

always be made by method (*a*), and when thus formed may be sublimed without decomposition. (*c*) Chlorides of Group I are best made by precipitation. (*d*) Metals soluble in HCl evolve H_2 and form chlorides. In these cases *ous*, not *ic* salts are formed. (*e*) Many chlorides may be prepared by interaction of $HgCl_2$ and the hot metal.

5. Solubilities. — Hydrogen chloride (gas) is readily soluble in water, as stated above (1). The solution is the hydrochloric acid of commerce. All chlorides except AgCl and Hg_2Cl_2 are soluble in water, TlCl, Cu_2Cl_2 and $PbCl_2$ being only slightly soluble. The concentration of Cl^- in a solution of $HgCl_2$ is insufficient to cause precipitation of $PbCl_2$. The chloride in a solution of green chromic chloride is incompletely precipitated by Ag^+ or Hg_2^{++}. Neither of these ions gives a chloride precipitate from a sulfuric acid solution of molybdenum oxychloride, MoO_2Cl_2. The chlorides of Sb^{+3}, Sn^{++} and Bi^{+3} require the presence of some free acid to keep them in solution. $AsCl_3$, PCl_3, $SbCl_5$ and $SnCl_4$ are liquids at room temperature. The first two are decomposed by H_2O with liberation of HCl: $AsCl_3 + 3\ H_2O = H_3AsO_3 + 3\ HCl$. Hydrochloric acid or high concentration of Cl^- increases the solubility of many chlorides, e.g., Pb, Hg, Ag, Sb, Au, Pt, Bi, Cu_2^{++}. This may be due, in part, to the "change of solvent," but the formation of a complex ion is largely responsible: $PbCl_2 + 2\ Cl^- = PbCl_4^{--}$. The chlorides of Th, Ba, Na, K and NH_4^+ are nearly insoluble in concentrated HCl.

Silver chloride is readily soluble in NH_4OH (separation from lead and mercurous chlorides), excess NaCN or sodium thiosulfate; easily decomposed by $Zn^\circ + H_2SO_4$. Lead chloride is soluble in the fixed alkali hydroxides.

Hydrochloric acid dissolves or transposes all insoluble oxalates, carbonates, hypophosphites, phosphates and sulfites. The sulfides of Fe^{++}, Mn and Zn are dissolved readily, those of Pb, Ag, Sb, Sn, Bi, Cu, Cd, Co and Ni if the acid is concentrated. As_2S_3 and As_2S_5 are insoluble in cold, concentrated HCl, very slowly soluble in the hot, concentrated acid. Mercuric sulfate is only partially transposed by HCl; $BaSO_4$ is unaffected. The sulfates of Pb, Hg_2^{++}, Sr and Ca are slowly but completely dissolved by hot concentrated HCl.

6. Reactions. — *A*. **With metals and their compounds.** — Hydrochloric acid acts upon the following metals, forming chlorides with evolution of H_2: Pb (slowly but completely), Sn, Cu (very slowly), Cd, Fe, Cr, Al, Co, Ni, Mn, Zn, and the metals of Groups V and VI. The metals Ag, Hg, As, Sb, Au, Pt and Bi are insoluble in HCl.

In general HCl is the best solvent for metallic oxides. It will dissolve all of the common oxides and hydroxides except (*a*) those of Group I metals, which are converted to insoluble chlorides, and (*b*) certain oxides which have been ignited: Cr_2O_3, Al_2O_3, Fe_2O_3, SnO_2, NiO_2. In most of these cases long-continued boiling will effect solution; Cr_2O_3, however, is particularly inert. Nitric acid is less effective than HCl as a solvent for the

four oxides. The solution of many higher oxides is accomplished with reduction of the metal to a lower valence: PbO_2 forms Pb^{++}, MnO_2 becomes Mn^{++}, Co_2O_3 yields Co^{++}, etc. (see below).

The following metallic compounds are attacked by HCl with reduction of the metal and evolution of Cl_2:

1. *Pb*, of valence greater than two, becomes $PbCl_2$.
2. As^{+5} becomes $AsCl_3$ in very concentrated HCl.
3. Bi^{+5} yields $BiCl_3$.
4. Cr^{+6} forms Cr^{+3}. Dry HCl does not reduce Cr^{+6} but combines with it to form chromyl chloride, CrO_2Cl_2 (used to detect Cl^- in the presence of Br^-).
5. With the exception of ferrates the salts of *Fe* are not reduced by HCl.
6. Co^{+3} forms Co^{++}.
7. Ni^{+4} yields Ni^{++}.
8. *Mn*, of valence greater than two, is reduced to Mn^{++}.

B. **With non-metals and their compounds.**

1. There is no reducing action with $H_2C_2O_4$, H_2CO_3, *HCN*, *HCNS*, $H_4Fe(CN)_6$ or $H_3Fe(CN)_6$.

2. HNO_2 forms chiefly NO and Cl_2. Nitric acid forms NO_2Cl and Cl_2, or NOCl and Cl_2, or merely NO_2 and Cl_2. When excess HCl is used the reaction is: $2\ HNO_3 + 6\ HCl = 2\ NO + 3\ Cl_2 + 4\ H_2O$. If dry HCl gas is passed into a cold mixture of concentrated H_2SO_4 and HNO_3 the reaction becomes: $2\ HCl + 2\ HNO_3 = 2\ H_2O + NO_2 + Cl_2$.

3. HCl does not reduce H_2SO_3 or H_2SO_4. Thiosulfates form the unstable $H_2S_2O_3$ which quickly decomposes (p. 507): $Na_2S_2O_3 + 2\ HCl = 2\ NaCl + S + SO_2 + H_2O$. The sulfates Ag_2SO_4 and Hg_2SO_4 are completely transposed by HCl; all others are more or less completely transposed with the exception of $BaSO_4$, which is practically unaffected.

4. With an excess of HCl, *hypophosphites*, *phosphites*, and *phosphates* are dissolved or transposed without reduction.

5. *Hypochlorous* acid forms Cl_2: $HClO + HCl = H_2O + Cl_2$. *Chloric* acid forms ClO_2, Cl_2O and Cl_2 in varying amounts. With HCl in excess the following reaction takes place: $KClO_3 + 6\ HCl = KCl + 3\ Cl_2 + 3\ H_2O$.

6. $KBrO_3$ is decomposed by boiling with HCl: $2\ KBrO_3 + 12\ HCl = 2\ KCl + Br_2 + 5\ Cl_2 + 6\ H_2O$.

7. HIO_3 reacts with HCl to form ICl_3 and Cl_2: $HIO_3 + 5\ HCl = ICl_3 + Cl_2 + 3\ H_2O$. There is no action in dilute solution.

7. Ignition. — The metal chlorides are generally more volatile than the other compounds of the same metals. Insoluble chlorides are readily transposed by fusion with Na_2CO_3: $PbCl_2 + Na_2CO_3 = PbO + 2\ NaCl + CO_2$. If charcoal is used as an ingredient of the fusion mixture, the metal is obtained: $2\ PbCl_2 + 2\ Na_2CO_3 + C = 2\ Pb + 4\ NaCl + 3\ CO_2$.

Heated in a bead of microcosmic salt, previously saturated with CuO in the inner blowpipe flame, chlorides impart a blue color to the outer flame, due to the copper chloride. Dry Na_2SO_4 at 150° is transposed by dry HCl. The silver halides heated with Bi_2S_3 on charcoal before the blowpipe give distinguishing colored incrustations: AgI, bright red; AgBr, deep yellow; AgCl, white.

8. Detection. — (*a*) If Ag^+ is added to an acid solution of Cl^- a curdy white precipitate of AgCl is formed, which darkens on exposure to light (cf. p. 175, 180). Traces of Cl^- give only an opalescence. Bromides, iodides and sulfides interfere with the test.

(*b*) Traces of free hydrochloric acid may be detected by boiling the solution with MnO_2 and collecting the distillate in a mixture of KI and starch to obtain the blue starch iodide. Larger amounts of HCl are usually separated by distillation without oxidation to Cl_2.

(*c*) The reaction with chromic anhydride is used to detect chloride, especially in the presence of bromide. Moisture must be absent.

$$2\,HCl + CrO_3 = CrO_2Cl_2 + H_2O$$

$$4\,NaCl + K_2Cr_2O_7 + 3\,H_2SO_4 = 2\,CrO_2Cl_2 + 2\,Na_2SO_4 + K_2SO_4 + 3\,H_2O$$

The brownish-red fumes from the chromyl chloride, CrO_2Cl_2, are easily seen. In case of doubt the distillate should be collected and a test for CrO_4^{--} applied: $CrO_2Cl_2 + 2\,H_2O = H_2CrO_4 + 2\,HCl$. The chlorides of Hg do not respond to the test since they are not transposed by H_2SO_4. The chlorides of Pb, Ag, Sb and Sn are so slowly transposed that the formation of CrO_2Cl_2 may escape detection.[1]

(*d*) Chloride in an insoluble chloride, e.g., AgCl, may be detected by digestion with Zn° and H_2SO_4. Metallic Ag is precipitated and Cl^- liberated. After filtration the usual tests for Cl^- may be applied to the filtrate.

9. Determination. — *Gravimetrically,* Cl^- is determined by precipitation as AgCl which is dried and weighed. *Volumetrically,* Cl^- may be precipitated by adding an excess of standard $AgNO_3$. The AgCl is filtered off and the Ag^+, in the filtrate, titrated with CNS^- using Fe^{+3} as an indicator. The total Ag^+ minus that recovered is the amount required to react with the chloride. A shorter and slightly less accurate method is to titrate the Cl^-, in a neutral solution, directly with standard $AgNO_3$ using a few drops of K_2CrO_4 as indicator.

[1] Cf. Comanducci, *Ch. Ztg.*, **35**, 540 (1911), *C.A.* **6**, 2903. Various other methods for the separation and detection of Cl^- are given later (§283). A very complete summary of the many methods for testing a mixture of the halides is given by Kunft, *Z. anal. Ch.*, **64**, 50 (1924), *C.A.* **18**, 2856. He particularly emphasizes the value of Vortmann's procedure which makes use of the fact that Na_3AsO_3 reacts with AgCl but not with AgBr or AgI.

§247. Hypochlorous Acid. HClO

1. Physical Properties. — Hypochlorous anhydride, Cl_2O, is a reddish-yellow gas[1] condensing near 0° to a blood-red liquid which boils at 3.8° under a pressure of 766 mm., The density at 22.3° and 728.6 mm. is 0.0034. Rise of temperature causes explosive decomposition into chlorine and oxygen. At 0° one volume of H_2O dissolves at least 200 volumes of Cl_2O. The reaction $Cl_2O + H_2O = 2\ HClO$ is said to be reversible. The acid, HClO, has not been isolated. Its aqueous solution smells like Cl_2O.[2] It decomposes more or less rapidly, depending upon the concentration and exposure to light. In a 0.25 *M* solution 3% of the acid decomposed in one month.[3] A cold, 25% solution is stable for only a short time; at 0° decomposition commences after a few hours.[4] Sunlight or diffuse daylight promotes the reaction: $5\ HClO = HClO_3 + 4\ HCl + O_2$.[5] The presence of a catalyst, as $Co(OH)_2$, markedly hastens the evolution of oxygen. HClO is a very weak, monobasic acid, even weaker than carbonic acid. There is apparently some evidence for its amphoteric ionization:

$$HClO \rightleftarrows H^+ + ClO^-$$

$$HClO \rightleftarrows Cl^+ + OH^-$$ [6]

The oxidation potential of ClO^- is lowest in alkaline solution. It increases with increasing concentration of H^+ but beyond the neutral point the stability decreases rapidly.[7]

3. Preparation. — Chlorine monoxide, Cl_2O, is readily prepared by the action of Cl_2 on HgO.[8] If a temperature of 0° is maintained the Cl_2O may be collected as a liquid. It is highly explosive. Cl_2O may also be prepared by the interaction of NH_2Cl and H_2O in the presence of anhydrous calcium chloride: $NH_2Cl + H_2O = NH_3 + HClO$; $2\ HClO = Cl_2O + H_2O$.[9]

For commercial purposes, as a bleaching agent and as a disinfectant, the most important hypochlorite is bleaching powder (§245) made by the action of Cl_2 on slaked lime. A practically pure solution of HClO may be made by distilling a solution of bleaching powder, one part; boric acid, two to three parts; and water, thirty parts.[10] Solutions containing up to 18% hypochlorite, as NaClO, are readily prepared by passing chlorine gas into a cold solution of NaOH: $2\ NaOH + Cl_2 = NaClO + NaCl + H_2O$. Only a small amount of chlorate is obtained if the temperature is low enough and an excess of NaOH maintained. The dilute solution (4%) widely sold today under the trade names "Chlorox," "Oxol," etc., is probably made by electrolysis of a solution of NaCl in a cell containing no diaphragm, i.e., one in which the Cl_2 evolved at the anode may react with the OH^- formed at the cathode. True Javelle[11] water, used as a bleach, is a dilute solution of KClO and KCl. Dakin's solution or the modification known as

[1] Goldschmidt, *Ber.*, **52**, 760 (1919).

[2] There is some difference of opinion as to whether the odor is that of Cl_2O or HClO itself.

[3] Billeter, *Helv. Ch. Acta*, **1**, 487 (1918).

[4] Goldschmidt, *Ber.*, **52**, 759 (1919).

[5] Allmand, *et al.*, *J. Ch. Soc.*, **127**, 822 (1925); **1927**, 655, state that the molecule, HClO, is light sensitive, while Benrath and Schaffganz, *Z. physik. Ch.*, **103**, 149 (1922), maintain that the ion ClO^- is decomposed: $2\ ClO^- = 2\ Cl^- + O_2$.

[6] Noyes and Wilson, *J. Am. Ch. Soc.*, **44**, 1630 (1922); Soper and Smith, *J. Ch. Soc.*, **1926**, 1582.

[7] Remington and Trimble, *J. Phys. Ch.*, **33**, 424 (1929); Hofmann and Ritter, *Ber.*, **47**, 2233 (1914), *C.A.* **8**, 3275.

[8] Cf. Gay-Lussac, *Compt. rend.*, **14**, 933 (1842).

[9] Marckwald and Wille, *Ber.*, **56**, 1323 (1923).

[10] Taylor, *J. Ch. Soc.*, **101**, 451 (1912); cf. Goldschmidt, *Ber.*, **52**, 753 (1919), *C.A.* **14**, 29.

[11] First prepared at Javelle, near Paris, France in 1792.

Dakin-Carrel solution, used to promote the healing of stubborn and infected wounds, is a 0.45% solution of $NaClO$.[1] Solid hypochlorites of the alkali and alkaline earth metals can be obtained by evaporation of their strongly alkaline solutions at low temperatures.[2]

5. Solubilities. — All hypochlorites are soluble in water and are decomposed by boiling.[3]

6. Reactions. — The hypochlorites are all unstable. They are decomposed by nearly all acids, including CO_2: $2\ Ca(ClO)_2 + 2\ CO_2 = 2\ CaCO_3 + 2\ Cl_2 + O_2$; $4\ NaClO + 4\ HCl = 4\ NaCl + 2\ Cl_2 + O_2 + 2\ H_2O$. They are very powerful oxidizing agents, acting, according to some investigators, as free chlorine. There seems, however, to be considerable justification for the statement that the action is due to oxygen rather than chlorine:

$$NaClO \rightarrow NaCl + O \text{ (active)}$$

$$Ca(ClO)_2 \rightarrow CaCl_2 + 2\ O \text{ (active)}$$ [4]

A hypochlorite heated in the presence of a catalyst forms ClO_3^- and Cl^-. The rate is increased if the system is made slightly acid.[5] A solution containing both Cl^- and ClO^- can be made to yield Cl_2 in almost any desired concentration by properly adjusting the acidity.

Chlorine monoxide, Cl_2O, reacts explosively with C, P, As and S, also with various metals and their compounds. Hypochlorous acid attacks some metals with liberation of hydrogen; others do not liberate a gas:

$$Mg^\circ + 2\ HClO = Mg(ClO)_2 + H_2$$

$$2\ Hg^\circ + 2\ HClO = HgO + HgCl_2 + H_2O$$

The oxides PbO, SnO, FeO, MnO, NiO and CoO are oxidized by HClO to PbO_2, SnO_2, Fe_2O_3, MnO_2, NiO_2 and Co_2O_3 respectively; Cr_2O_3 in alkaline medium forms CrO_4^{--}. As, P and S in their lower valences are oxidized to AsO_4^{-3}, PO_4^{-3} and SO_4^{--}; Sb^{+3} becomes Sb^{+5}; Sn^{++} changes to Sn^{+4}; Mn^{++} forms MnO_2 except in the presence of Ag^+, Cu^{++}, etc., which assist the oxidation to MnO_4^-.[6]

[1] Cf. Davis and Langenham, *J. Am. Pharm. Assoc.*, **13**, 131, 222 (1924).

[2] Ochi, *Trans. Am. Electroch. Soc.*, **49**, 141 (1926). "H T H" is said to be true calcium hypochlorite, $Ca(ClO)_2$. The commercial article contains 60%–65% "available chlorine" and sufficient $Ca(OH)_2$ to stabilize the system. Concerning crystalline NaClO see: Applebey, *J. Ch. Soc.*, **115**, 1106 (1919).

[3] Distillation of the acid without decomposition is easily effected, however, from a sufficiently dilute solution.

[4] For another explanation of the chemical behavior of hypochlorites see: Justin-Miller, *J. pharm. Ch.*, **20**, 113 (1919), *C.A.* **13**, 2645.

[5] For the kinetics of the thermal decomposition of NaClO see: Giordani and Mattias (*C.A.* **23**, 2636); cf. Sanfourche and Gardent, *Bull. soc. ch.*, [4] **35**, 1092 (1924); Foerster and Dolch, *Z. Elektroch.*, **23**, 137 (1917).

[6] Cf. Dixon and White, *J. Ch. Soc.*, **1927**, 1469.

Hypochlorous acid reacts with H_2O_2 to form HCl and O_2:

$$HClO + H_2O_2 = HCl + O_2 + H_2O$$

Thiocyanates are decomposed to give CNCl and SO_4^{--}; HNO_2 becomes HNO_3; H_2S and H_2SO_3 form H_2SO_4, while $Na_2S_2O_3$ yields a mixture of Na_2SO_4 and $Na_2S_4O_6$: $5\ NaClO + 3\ Na_2S_2O_3 = 5\ NaCl + 2\ Na_2SO_4 + Na_2S_4O_6$. If HCl is added to a solution of HClO evolution of Cl_2 ensues: $HClO + HCl = Cl_2 + H_2O$; if a chloride is used there is a simultaneous formation of a chlorate: $6\ HClO + NaCl = NaClO_3 + 3\ Cl_2 + 3\ H_2O$.[1] Bromides react with HClO to form bromates. The same is true of iodides.

8. Detection. — Although silver hypochlorite is soluble in H_2O, it decomposes very quickly, hence on adding Ag^+ to a solution of ClO^- a white precipitate of AgCl forms: $3\ NaClO + 3\ AgNO_3 = 2\ AgCl + AgClO_3 + 3\ NaNO_3$. When KClO is shaken with Hg°, yellowish red Hg_2OCl_2 is formed; the other potassium salts of chlorine, i.e., KCl, $KClO_2$, $KClO_3$ and $KClO_4$, have no action on Hg°. An indigo solution is decolorized by ClO^- while $KMnO_4$ is not affected. If AsO_3^{-3} is present the indigo solution is not attacked until the arsenite is all oxidized.

9. Determination. — *Gravimetrically*, hypochlorites may be reduced to chloride which is precipitated, dried and weighed as AgCl. Usually a *volumetric* method is employed. (*a*) An excess of KI may be added and the I_2 titrated with $Na_2S_2O_3$. (*b*) The ClO^- may be titrated directly with KI in a neutral solution using starch as indicator. (*c*) The ClO^- may be titrated with Na_3AsO_3, the endpoint being determined electrometically.[2]

§248. Chlorous Acid. $HClO_2$

The anhydride, Cl_2O_3, has not been isolated and the free chlorous acid is known only in solution. It has an intense yellow color and is unstable except in very dilute solution.[3] At 0° decomposition starts in about ten minutes: $4\ HClO_2 = 3\ ClO_2 + Cl + 2\ H_2O$. The color and odor of ClO_2 are easily recognized. The chlorite ion, ClO_2^-, is said to decompose in two ways yielding O_2 and Cl^- or ClO_3^- and Cl^-. Chlorous acid is monobasic, stronger than carbonic acid and a strong oxidant.[4] The preparation of a chlorite is effected by the interaction of chlorine dioxide, ClO_2, and the hydroxide of the metal: $2\ ClO_2 + 2\ OH^- = ClO_2^- + ClO_3^- + H_2O$.[5] Many of the salts have been isolated but practically all are very unstable, some exploding when jarred.[6] They are soluble in water with the exception of $Pb(ClO_2)_2$ and $AgClO_2$ which are slightly soluble, 0.035 g. and 0.17 g./100 cc. of H_2O at 0°, respectively.

In dilute acid solution ClO_2^- is a strong oxidant, changing AsO_3^{-3} to AsO_4^{-3}, Mn^{++}

[1] Under special conditions: $NaCl + HClO = NaOH + Cl_2$.

[2] Cf. Ditz and May, *Z. anal. Ch.*, **79**, 371 (1930), *C.A.* **24**, 1820.

[3] Bray, *Z. anorg. allgem. Ch.*, **48**, 233 (1906), obtained a fairly stable solution of ClO_2^- by adding an excess of $NaHCO_3$.

[4] Bray, *loc. cit.*, states that ClO_2^- is not a strong oxidant but that $HClO_2$ is.

[5] Cf. Laséque, *Compt. rend.*, **155**, 158 (1912), *C.A.* **6**, 3376; Bruni and Levi (*C.A.* **10**, 570).

[6] Gmelin, 8th ed., No. 6, p. 300, gives a list of the known salts.

to MnO_2 (MnO_4^- becomes MnO_2 also), Fe^{++} to Fe^{+3}, etc. Among the non-metals CNS^- forms SO_4^{--} and HCN: $2\,NaCNS + 3\,NaClO_2 + 2\,H_2O = 2\,NaHSO_4 + HCN + 3\,NaCl$; sulfides, sulfites and thiosulfates are changed to sulfates; HClO yields ClO_2 and chlorine, but NaClO forms $NaClO_3$ and NaCl; bromides in neutral solution are not affected, in acid solution Br_2 is liberated; iodides react slowly in neutral solution to form I_2,[1] in acid solution HIO_3 is obtained.

The detection of ClO_2^- may be effected as follows: (*a*) a concentrated solution of a chlorite gives a white precipitate with Ag^+; (*b*) $KMnO_4$ is changed to MnO_2; (*c*) an indigo solution is decolored even in the presence of AsO_3^{-3} (distinction from ClO^-); (*d*) ClO_2^-, when slightly acidified, gives a transient amethyst tint to a solution of $FeSO_4$.

The determination of ClO_2^- *volumetrically* involves addition of KI, acidification and titration of the I_2 with $Na_2S_2O_3$.[2]

§249. Chloric Acid. $HClO_3$

1. Physical Properties. — A solution of chloric acid may be evaporated in a vacuum until its density is 1.282 at 14°. The composition is then $HClO_3{\cdot}7H_2O$, i.e., 40.1% $HClO_3$. The system is fairly stable but decomposition slowly ensues. Further decomposition results in a rapid evolution of Cl_2 and O_2: $8\,HClO_3 = 4\,HClO_4 + 3\,O_2 + 2\,Cl_2 + 2\,H_2O$. Its solution in the cold is colorless and odorless, first reddening, then bleaching, litmus. It is a strong acid, much less stable than H_2SO_4, $HClO_4$ or its salts, but more stable than HNO_3. Chloric acid decomposes in three ways, into (*a*) $HClO_4$ and HCl, (*b*) HCl and O_2, and (*c*) ClO_2 and O_2:

$$\text{(a)}\ 4\,HClO_3 = 3\,HClO_4 + HCl$$
$$\text{(b)}\ 2\,HClO_3 = 2\,HCl + 3\,O_2$$
$$\text{(c)}\ 4\,HClO_3 = 4\,ClO_2 + O_2 + 2\,H_2O$$

Chloric acid is a strong oxidizing agent, hence its use as a chlorate in matches, fireworks, explosives, etc.

3. Preparation. — Chlorates are easily prepared by (a) passing Cl_2 into the hot solution of an alkali (not NH_4OH) or alkaline earth hydroxide; (b) electrolysis of a hot chloride solution in a cell without a diaphragm; (c) oxidation of hypochlorites. Repeated crystallization separates the chlorate from any chloride that may contaminate the product. A solution of $HClO_3$ may be prepared by adding the calculated amount of H_2SO_4 to a solution of $Ba(ClO_3)_2$ and filtering off the $BaSO_4$ precipitated.

5. Solubilities. — All chlorates are soluble in water, those of Hg, Bi and Sn requiring a little free acid. Mercurous and ferrous chlorates are very unstable. Potassium chlorate is the least soluble of the stable metallic chlorates, lithium chlorate one of the most soluble; 6.6 g. and 315 g., respectively, per 100 cc. of water at 18°.

6. Reactions. — *A*. **With metals and their compounds.** — Chloric acid attacks Mg°, evolving hydrogen and forming a chlorate only; with Zn°, Fe°, Sn° and Cu° some chloride is also formed. Using Zn° and dilute H_2SO_4 reduction to Cl^- is complete, but sodium amalgam has no effect;[3] with the zinc-copper couple[4] reduction to Cl^- is rapid and complete. Hot,

[1] Kolthoff, *Rec. trav. ch.*, **41**, 741 (1922).

[2] Schleicher and Wesly, *Z. anal. Ch.*, **65**, 408 (1924–5), determine the endpoint electrometically.

[3] Enfield, *J. Ch. Soc.*, **97**, 2441 (1910).

[4] Metallic Zn with a thin coating of copper oxide.

concentrated $HClO_3$ attacks all metals. Their oxides and hydroxides form chlorates provided a chlorate of the metal concerned can be formed. Free chloric acid is a very strong oxidant. When an excess of the reductant is used the ClO_3^- becomes Cl^-. In general metal ions of lower valence, as Hg_2^{++}, Sn^{++}, Fe^{++}, Ti^{+3}, are oxidized to the higher state; AsO_3^{-3} is slowly changed to AsO_4^{-3} in strongly acid solution; $MnSO_4$ is not oxidized by ClO_3^- alone (distinction from BrO_3^- and IO_3^-), but in the presence of HNO_3 rapid conversion to MnO_2 takes place. Salts of Pb, Co and Ni do not appear to be oxidized on boiling with $KClO_3$ and HNO_3.

B. **With non-metals and their compounds.**

1. *$H_2C_2O_4$* or *oxalate* ion forms CO_2 and varying amounts of Cl_2 and Cl^-. Heat and excess of the reductant favor the formation of Cl^-. *HCNS* forms H_2SO_4, HCN and HCl. *$H_4Fe(CN)_6$* first becomes $H_3Fe(CN)_6$ which decomposes, if an excess of ClO_3^- is present. *H_2O_2*, in presence of a small amount of HNO_3, completely reduces ClO_3^- to Cl^- [1] (distinction from BrO_3^- and IO_3^-).

2. *HNO_2* is oxidized to HNO_3 which has no effect on ClO_3^-.[2]

3. *PH_3*, *H_3PO_2* and *H_3PO_3* form H_3PO_4. The reaction may take place explosively.

4. *Sulfur* compounds in which S has a valence less than six are oxidized to SO_4^{--}. Under some conditions free sulfur may be liberated but it is ultimately changed as indicated. *Persulfates* oxidize ClO_3^- to ClO_4^-.[3]

5. *HCl* in excess reduces ClO_3^- to Cl_2: $ClO_3^- + 5\ Cl^- + 6\ H^+ = 3\ Cl_2 + 3\ H_2O$. NaCl warmed with $HClO_3$ evolves Cl_2 leaving only $NaClO_3$.

6. *HBr* slowly forms Br_2 and HCl. KBr warmed with $HClO_3$ evolves Br_2 leaving only $KClO_3$. Any reaction between *bromine* and ClO_3^- is slow and probably complicated.

7. *Iodine* heated with $KClO_3$ forms KIO_3 and ICl_3.[4] When *KI* is added to $KClO_3$ in the presence of a mineral acid, I_2 is liberated but if the acid is acetic no I_2 is obtained even after standing for some hours[5] (distinction from IO_3^-).

7. Ignition. — All chlorates are decomposed by heat into chlorides and O_2: $2\ KClO_3 = 2\ KCl + 3\ O_2$. Some perchlorate is usually formed as an intermediate product: $2\ KClO_3 = KClO_4 + KCl + O_2$. In some cases an oxide may be formed: $2\ Ca(ClO_3)_2 = 2\ CaO + 2\ Cl_2 + 5\ O_2$. In the presence of various metallic oxides, etc., the oxygen is separated more easily, the oxide remaining unchanged; with MnO_2 decomposition takes place at about 200°; Fe_2O_3, CuO, PbO_2 or platinum black, may be used instead of MnO_2. If a

[1] Jannasch and Jahn, *Ber.*, **38**, 1577, 1581 (1905).
[2] For the action of NH_4NO_3 on $KClO_3$ see: Salvadori, *Ann. ch. applicata*, **6**, 115 (1916), *C.A.* **10**, 3041.
[3] Bennett and Mack, *Trans. Am. Electroch. Soc.*, **29**, 323 (1916).
[4] Lamb, *et al.*, *J. Am. Ch. Soc.*, **42**, 1636 (1920).
[5] Gibson and Grieb, *Analyst*, **32**, 380 (1907).

chlorate is rapidly ignited some Cl_2 is given off. When triturated or heated with combustibles as charcoal, sulfur, sulfites, cyanides, thiosulfates, hypophosphites, finely divided metals, etc., the reaction is likely to be explosive. The explosion is more violent than with a similar mixture containing nitrate in place of the chlorate.

Alkali chlorates when fused with an alkali or an alkali carbonate and a free metal or a lower oxide, or salt of a metal, generally oxidize it to a higher oxide, or to a salt of higher valence, while the chlorate becomes a chloride.

(1) $3\,Mn_3O_4 + 18\,KOH + 5\,KClO_3 = 9\,K_2MnO_4 + 5\,KCl + 9\,H_2O$
(2) $2\,CrCl_3 + 10\,NaOH + NaClO_3 = 2\,Na_2CrO_4 + 7\,NaCl + 5\,H_2O$
(3) $3\,As_4 + 36\,KOH + 10\,KClO_3 = 12\,K_3AsO_4 + 10\,KCl + 18\,H_2O$
(4) $3\,Pb_3O_4 + Na_2CO_3 + 2\,NaClO_3 = 9\,PbO_2 + 2\,NaCl + Na_2CO_3$
(5) $6\,CoCl_2 + 12\,KOH + KClO_3 = 3\,Co_2O_3 + 13\,KCl + 6\,H_2O$
(6) $3\,K_2C_4H_4O_6 + 5\,KClO_3 = 5\,KCl + 3\,K_2CO_3 + 9\,CO_2 + 6\,H_2O$
(7) $3\,Pb(H_2PO_2)_2 + 18\,KOH + 5\,KClO_3 = 3\,PbO_2 + 6\,K_3PO_4 + 5\,KCl + 15\,H_2O$
(8) $ZnI_2 + K_2CO_3 + 2\,KClO_3 = ZnO + 2\,KIO_3 + 2\,KCl + CO_2$
(9) $3\,K_2S_5O_6 + 12\,K_2CO_3 + 10\,KClO_3 = 15\,K_2SO_4 + 10\,KCl + 12\,CO_2$

8. Detection. — (*a*) Chloric acid, like nitric, decolors indigo solution and gives colors with brucine, diphenylamine, paratoluidine and phenol, similar to those formed by HNO_3. (*b*) Upon ignition a chloride is left: $2\,KClO_3 = 2\,KCl + 3\,O_2$. (*c*) ClO_3^- is changed to Cl^- by a reducing agent: $2\,KClO_3 + 6\,Zn + 7\,H_2SO_4 = 6\,ZnSO_4 + K_2SO_4 + 2\,HCl + 6\,H_2O$; $2\,KClO_3 + 6\,H_2SO_3 = 2\,HCl + 5\,H_2SO_4 + K_2SO_4$. The resulting HCl is identified as usual. Chlorides, if originally present, should be removed by silver nitrate.

9. Determination. — Chlorate may be reduced to chloride which is precipitated, dried and weighed as AgCl. *Volumetrically,* ClO_3^- may be treated with KI in an acid solution and the liberated I_2 titrated with $Na_2S_2O_3$.[1] More satisfactory is the direct titration of ClO_3^- with Ti^{+3}.[2]

§250. Perchloric Acid.[3] $HClO_4$

1. Physical Properties. — Pure perchloric acid is a colorless, oily liquid. It is volatile but cannot be distilled at atmospheric pressure without decomposition, often with explosive violence. At 16° under 18 mm. pressure it boils undecomposed;[4] by extrapolation the boiling point at 760 mm. pressure is 130°.[5] The melting point is − 112°;[6]

[1] Taylor, *J. Soc. Dyers Colourists*, **32**, 66 (1916).
[2] For other methods see, Gmelin, 8th ed., No. 6, p. 354–62.
[3] A good discussion of this compound, including its preparation and analytical uses, may be found in a pamphlet prepared by G. Frederick Smith, "Perchloric Acid," The G. Frederick Smith Chemical Company, Columbus, Ohio, 1931. Cf. Roth, "Zur Kenntnis der Perchlorate." Dissert. München (1910).
[4] Van Wyk, *Z. anorg. allgem. Ch.*, **48**, 34 (1906).
[5] Hantzsch, *Ber.*, **60**, 1940 (1927).
[6] Van Wyk, *loc. cit.*

density, 1.7676 at 20°. It produces very painful wounds that are slow to heal. At temperatures approximately that of liquid air perchloric acid will keep indefinitely, but at ordinary temperatures, especially when exposed to light, it gradually decomposes and ultimately explodes. It is, therefore, a decidedly unsafe compound to prepare or use. The dilute acid is very stable, not being easily reduced. It does not bleach, but merely reddens blue litmus paper.

2. Occurrence. — The free acid is not found in nature. Traces of the potassium salt occur in Chile saltpeter. Neither the acid nor its salts have any extended commercial uses. Certain of the salts are very efficient drying agents, e.g., magnesium perchlorate,[1] barium perchlorate, etc.

3. Preparation. — Due to its dangerous nature anhydrous perchloric acid is prepared only for research purposes.[2] A 70% solution is readily obtained without hazard. The starting material is ammonium perchlorate made from the sodium salt which is a by-product of the electrolytic preparation of sodium chlorate. A hot solution of NH_4ClO_4 containing some HNO_3 is treated with dilute HCl. The aqua regia formed oxidizes the NH_4^+ leaving a dilute solution of $HClO_4$ containing a slight excess of the reagents. These are removed by boiling to a temperature of about 200° after which the residual liquid is distilled at 60°–95° under a pressure of 2–7 mm. The distillate will contain 70%–73.6% $HClO_4$ and have a density of 1.66–1.71.[3]

5. Solubilities. — Perchloric acid and all of its salts are readily soluble in water[4] and all of the latter are deliquescent except NH_4ClO_4, $KClO_4$, $Pb(ClO_4)_2$ and $HgClO_4$. Potassium perchlorate dissolves to the extent of 0.75 g. at 0° and 21.8 g. at 100° per 100 cc. of H_2O.[5] It is particularly insoluble in alcohol especially if a small amount of $HClO_4$ is present (distinction from $NaClO_4$[6] which dissolves to the extent of 209.6 g./100 cc. of H_2O at 25°).

6. Reactions. — Perchloric acid, in some of its properties, is similar to sulfuric acid. When hot and concentrated it is a very powerful oxidizing agent. A cold, dilute solution, however, is decidedly inert. As a solvent it reacts with Fe°, Zn° and some other metals to form a solution of the perchlorate with liberation of H_2. Oxides are readily attacked under suitable conditions, e.g., ignited Cr_2O_3 is easily dissolved.[7] Aqueous $HClO_4$ is not reduced by HCl, H_2S, SO_2, Fe^{++}, etc. Iodine is oxidized to HIO_4 with liberation of Cl_2: $I_2 + 2\,HClO_4 = 2\,HIO_4 + Cl_2$. A solution of indigo is not decolored by $HClO_4$ even after the addition of HCl (dis-

[1] Willard and Smith, *J. Am. Ch. Soc.*, **44**, 2255 (1922).

[2] Roscoe, *J. Ch. Soc.*, **16**, 84 (1863), has prepared the pure acid.

[3] See especially Willard, *J. Am. Ch. Soc.*, **34**, 1480 (1912). Mathers and Aldred, *Trans. Am. Electroch. Soc.*, **42**, 285 (1922), have prepared perchlorates by heating chlorates. Mack, *J. Phys. Ch.*, **21**, 238 (1917), has recommended the oxidation of ClO_3^- with persulfate.

[4] Perchloric acid forms a number of hydrates for a discussion of which see: Gmelin, 8th ed., No. 6, p. 372, *et seq.*

[5] For the solubility of the alkali and alkaline earth perchlorates in water and various alcohols at 25° see: Willard and Smith, *J. Am. Ch. Soc.*, **45**, 286–97 (1923).

[6] A bibliography of the applications of this point is given by Skinner and Collins, U. S. Dept. Agr., Bur. Ch. Bull., **153** (1912).

[7] For the preparation and properties of some perchlorates (Ni, Co, Cr, etc.) see: Goldblum and Terlikowski, *Bull. soc. ch.*, [4] **11**, 103 (1912).

tinction from all other oxyacids of chlorine). It is not reduced by the Zn-Cu couple (distinction from chlorate).

7. Ignition. — Perchlorates when strongly ignited evolve O_2 and leave a chloride.

8. Detection. — (*a*) In the presence of other chlorine compounds, ClO^-, ClO_2^- and ClO_3^- may be reduced to Cl^- by boiling with the Zn-Cu couple or HCl. The Cl^- may be removed as AgCl, the filtrate evaporated to dryness and the residue fused with Na_2CO_3. An aqueous extract of the melt will give a good test for Cl^- if a perchlorate was in the original sample. (*b*) ClO_4^- may be detected by precipitation as $KClO_4$. (*c*) An HCl solution of α-phenyl-β-diethylaminoethyl-*p*-nitrobenzoate gives an insoluble precipitate with ClO_4^- (0.12 g./100 cc. H_2O at 25°). The test is applicable in the presence of Cl^-, Br^-, ClO_3^-, IO_3^-, SO_4^{--}, CO_3^{--}, etc.[1] (*d*) Many of the alkaloids form insoluble perchlorates among which that obtained with strychnine sulfate is perhaps the least soluble.[2]

9. Determination. — (*a*) In the absence of other oxidizing agents ClO_4^- may be reduced with an excess of $Ti_2(SO_4)_3$ and the excess titrated with $KMnO_4$.[3] (*b*) ClO_4^- may be reduced to Cl^- which is determined as usual. (*c*) Precipitation with nitron[4] and as $KClO_4$[5] have also been suggested.

§251. Bromine (Gr. *bromos* = stench). Br = 79.916. Atomic No. 35. Valence 1 and 5. Discovered by Balard in 1825.

1. Physical Properties. — Density, 3.121 at 20°;[6] melting point, − 7.3°;[7] boiling point, 58.8° ± 0.1° at 760 mm.;[8] vapor pressure at 23.45°, 200 mm.; critical temperature, 311°; critical pressure, 102 atmospheres. At ordinary temperatures bromine is a brown-red, intensely corrosive liquid, freely evolving brown vapors of a suffocating odor somewhat similar to that of chlorine.

2. Occurrence. — Bromine is not found free in nature. It occurs as the bromide in sea water (0.188%), in the mother liquor or bittern left after removal of the NaCl from deep well brines (Michigan, Ohio and West Virginia),[9] and in the potash deposits of Germany and France. The world's production of bromine in 1930 was about 6400 tons, of which the United States, chiefly those mentioned above, contributed 3800 tons, Germany, 2000 tons, and France, 565 tons.[10] The bromine marketed in the United States during 1930 was about 8.5 million pounds, valued at 25 cents a pound and used chiefly as ethylene bromide in "ethyl" gasoline to insure volatilization of the lead as $PbBr_2$.

[1] Marvel and du Vigneaud, *J. Am. Ch. Soc.*, **46**, 2661 (1924).
[2] Denigès, *Ann. ch. anal. ch. appl.*, **22**, 127 (1917).
[3] Spitalsky and Jofa, *Z. anorg. allgem. Ch.*, **169**, 309 (1928); cf. König, *Ibid.*, **120**, 48 (1922).
[4] See: Loebich, *Z. anal. Ch.*, **68**, 34 (1926); Vürthein, *Rec. trav. ch.*, **46**, 97 (1927).
[5] Cf. Loebich, *loc. cit.*; Arndt and Nachtwey, *Ber.*, **59**, 446, 1072 (1926).
[6] Richards, *Z. physik. Ch.*, **49**, 18 (1904).
[7] U. S. Bur. Stds. Cir. 35.
[8] Bouzat and Leluan, *Compt. rend.*, **178**, 637 (1924).
[9] The Midland, Michigan brine is said to contain about 0.1% bromine.
[10] Mineral Ind., **1930**.

3. Preparation. — In the *laboratory* bromine may be obtained from (*a*) KBr and $KBrO_3$, (*b*) KBr and $K_2Cr_2O_7$, (*c*) KBr and MnO_2, and H_2SO_4. *Commercially*, this element is secured principally from the salt well bitterns:[1] (*a*) by anodic oxidation, the Br_2 being blown out of the solution by CO_2-free air and absorbed in Fe, Zn or Cu, or in NaOH, $Ca(OH)_2$, Na_2CO_3 or $NaHCO_3$, etc.; (*b*) by treatment with a chlorate and H_2SO_4; by reaction with (*c*) Cl_2; (*d*) bleaching powder; or (*e*) MnO_2 and H_2SO_4, the recovery being accomplished as indicated in (*a*).

$$MgBr_2 + MnO_2 + 2\ H_2SO_4 = MgSO_4 + MnSO_4 + Br_2 + H_2O$$

Recently the removal of bromine from sea water has been advocated.[2] The bromine is liberated by means of chlorine and taken up with aniline.

4. Oxides and Acids. — Apparently bromine does not form oxides of any importance; Br_2O has been reported as resulting from the interaction of HgO and bromine vapor, $(Br_3O_8)_n$ from the combination of Br_2 and ozone.[3] Among the acids, hydrobromic, HBr, hypobromous, HBrO, and bromic, $HBrO_3$, are well known. The formation of bromites has been reported[4] and the non-existence of perbromic acid has been emphasized.[5] HBr and $HBrO_3$ will be discussed in separate sections (§§252–3). Hypobromous acid is prepared similarly to, and in properties resembles, hypochlorous acid. It is used even less than that reagent. It is fairly stable but slowly decomposes according to the two reactions:

$$(1)\ 5\ HBrO \rightarrow HBrO_3 + 2\ H_2O + 2\ Br_2$$

$$(2)\ 4\ HBrO \rightarrow O_2 + 2\ Br_2 + 2\ H_2O.$$[6]

The hypobromite ion may be detected by adding it dropwise to an alkaline solution of urea. After introducing a slight excess of 5% $HgCl_2$ and filtering, 4–5 cc. of 50% NaOH added to the filtrate will produce Hg°.[7]

5. Solubilities. — Bromine dissolves in water to form a 3.21% solution at 20°. The system formed is probably represented by the equation: $Br_2 + H_2O \rightleftarrows HBr + HBrO$. The HBrO slowly decomposes leaving HBr: $2\ HBrO = 2\ HBr + O_2$. Bromine is much more soluble in HCl, HBr, KBr, $BaCl_2$, $SrCl_2$ and in solutions of many other salts than in water alone. It is soluble in various organic liquids, e.g., carbon tetrachloride, carbon disulfide, chloroform, ether and alcohol, and may be readily extracted from its aqueous solution by these solvents.

6. Reactions. — *A*. **With metals and their compounds.** — Anhydrous bromine does not react readily with many metals. In the presence of water, however, it is a strong oxidizing agent. It unites directly with Au°, Pt°, and all ordinary metals to form bromides. In general, the valence of higher oxides is not affected by bromine but that of lower oxides is raised. Silver salts form precipitates of the bromide and bromate:

$$6\ AgNO_3 + 3\ Br_2 + 3\ H_2O = 5\ AgBr + AgBrO_3 + 6\ HNO_3$$

[1] Cf. Dow, *Chem. Eng.*, **27**, 258 (1919). For a summary of the patent literature, see, Gmelin, 8th ed., No. 7, p. 41, *et seq.* (1931).

[2] Stine, *Ind. Eng. Ch.*, **21**, 434 (1929); Dyson, *Ch. Age* (London), **23**, 450 (1930). Cf. U. S. Pat. 1,662,305 and 1,662,355.

[3] Cf. Gmelin, 8th ed., No. 7, p. 285.

[4] Clarens, *Compt. rend.*, **156**, 1998 (1913), *C.A.* **7**, 3578.

[5] Robertson, *Ch. News*, **106**, 50 (1912).

[6] Pollak and Doktor, *Z. anorg. allgem. Ch.*, **196**, 89 (1931), *C.A.* **25**, 2067.

[7] Pisani, *Ann. ch. applicata*, **18**, 555 (1928), *C.A.* **23**, 1841.

If the system is kept cold, hypobromite, not the bromate, is formed: $AgNO_3 + Br_2 + H_2O = AgBr + HBrO + HNO_3$. Many ions are oxidized by bromine with the formation of Br^-. The reaction is less violent than with chlorine. In an acid or alkaline solution, the following are oxidized to a higher valence: Hg_2^{++} to Hg^{++}, As^{+3} to As^{+5} (AsH_3 forms H_3AsO_3 first; an excess of Br_2 is required for the oxidation to arsenate), Sb^{+3} to Sb^{+5}, Sn^{+2} to Sn^{+4}, Cu_2^{++} to Cu^{++}. In an alkaline mixture only, the following changes may be effected: Pb^{++} to PbO_2, Bi^{+3} to BiO_3^-, Cr^{+3} to CrO_4^{--}, Co^{++} to Co^{+3}, Ni^{++} to Ni^{+4}, Mn^{++} to MnO_2.

B. **With non-metals and their compounds.** — Bromine, like chlorine, reacts with cold fixed alkali and alkaline earth hydroxides to form a bromide and a hypobromite: $2\,NaOH + Br_2 = NaBr + NaBrO + H_2O$. If the system is hot a bromate is obtained in place of the hypobromite.

1. *$H_2C_2O_4$* forms CO_3^{--} and Br^- in an alkaline system. An excess of hot saturated oxalic acid solution changes Br_2 to HBr.

CNS^- forms, among other products, SO_4^{--} and a bromide in acid or alkaline mixture.

Ferrocyanides are oxidized to $Fe(CN)_6^{-3}$ in acid or alkaline solution.

2. *Nitrites* are oxidized to NO_3^-. *Peroxides* react violently with Br_2, oxygen being evolved: $H_2O_2 + Br_2 = HBr + O_2$.

3. *Phosphorus* compounds, in which the valence of phosphorus is lower than five, react with Br_2 to form PO_4^{-3}. The element, P°, forms PBr_3 or PBr_5, depending upon the relative amounts of the reactants present. The phosphorus bromides are decomposed by H_2O to form HBr and the corresponding acids of phosphorus.

4. *Sulfur* compounds in which the valence of sulfur is lower than six are oxidized to SO_4^{--} by Br_2: $Na_2S_2O_3 + 4\,Br_2 + 5\,H_2O = 2\,NaHSO_4 + 8\,HBr$ (distinction from I_2).

5. *Chlorine* in many compounds can be partially replaced by bromine if the chloride is digested with bromine water. Under ordinary conditions chlorates or perchlorates are not affected by bromine water.

6. *Hypobromites*, boiled in an alkaline solution, become bromates.

7. *Iodine* reacts with Br_2 to form IO_3^- and Br^- in an alkaline system. *Iodides* in acid solution become free iodine, in alkaline media, IO_3^- and Br^- are obtained.

7. **Ignition.** — Warming drives off all the bromine from its solutions in H_2O or other solvents. Heat favors all reactions with Br_2.

8. **Detection.** — Bromine is usually detected by shaking its aqueous solution with CCl_4 or CS_2. The extract is colored reddish yellow to dark brown, depending upon the amount of bromine present. Starch solution gives a yellow color with Br_2, but the reaction is less delicate. Bromine changes fluorescein into eosin, which is the color of red ink. This is a very

delicate test for Br_2.[1] Many other organic compounds have also been suggested as rosaniline bisulfite,[2] strychnine,[3] Hoffmann's violet,[4] etc. Air containing bromine vapor, one part in 100,000, can be detected readily, if breathed, by its irritating effect on the mucous membrane of the nose.

9. Determination. — Bromine may be converted to a bromide which is determined by (*a*) precipitation as AgBr, dried and weighed, (*b*) titrated with $AgNO_3$ by the Volhard method. An excess of KI may be added to a solution of Br_2 and the liberated iodine titrated with $Na_2S_2O_3$. Bromine may also be titrated in alkaline solution with standard arsenite.

§252. Hydrobromic Acid. HBr

1. Physical Properties. — Hydrogen bromide is a colorless gas. If solidified it *melts* at $-86.86° \pm 0.05°$ and *boils* at $-66.72° \pm 0.05°$.[5] The *density* at 0° and 760 mm. is 3.64445 g./l.;[6] *critical temperature*, 89.80°; *critical pressure*, about 84 atmospheres. The aqueous solution, known as hydrobromic acid, forms a constant boiling mixture at 126° and contains 47% HBr corresponding very closely to $HBr{\cdot}5H_2O$. A 20% solution has a density of 1.1579 at 20°.

2. Occurrence. — Hydrobromic acid is not found free in nature. In combination as a bromide it exists in sea water and in some minerals.

3. Preparation. — (*a*) Many patents have been granted for the preparation of HBr based on the interaction of H_2 and Br_2 in the presence of a suitable catalyst, e.g., platinum.[7] (*b*) H_2S is added to a solution of bromine in water until the yellow color disappears. The solution is then distilled, the first and last portions of the distillate being rejected due to contamination with H_2S and H_2SO_4 respectively. (*c*) SO_2 may be used in place of H_2S: $SO_2 + Br_2 + 2\,H_2O = H_2SO_4 + 2\,HBr$. (*d*) H_2SO_4 or H_3PO_4 is added to a concentrated solution of NaBr. Upon heating the mixture HBr is driven off. It may be absorbed in H_2O. (*d*) Bromine vapor is passed over heated aluminum to form $AlBr_3$ which is then converted to the hexahydrate, $AlBr_3{\cdot}6H_2O$. When heated this product liberates HBr and H_2O leaving a residue of Al_2O_3.

5. Solubilities. — At 20° and 760 mm. 100 g. of saturated aqueous solution will contain 49 g. of HBr, or 100 cc. of water at 25° will dissolve 193 g. of HBr. Silver and mercurous bromide are insoluble in water, lead bromide sparingly soluble; all other bromides are soluble. The Group I bromides are less soluble than the corresponding chlorides. The presence of an excess of Br^- appreciably increases their solubility. In *alcohol* the alkali bromides are slightly soluble; $CaBr_2$ and $HgBr_2$ soluble, Hg_2Br_2 insoluble. AgBr is less soluble in NH_4OH than is AgCl.

6. Reactions. — *A.* **With metals and their compounds.** — Hydrobromic acid dissolves many metals with the formation of bromides and evolution

[1] Swarts, *Bul. Acad. roy. Belg.*, [3] **17**, 359 (1889); Lorenz, *et al.*, *Z. anorg. allgem. Ch.*, **136**, 90–4 (1924).

[2] Denigès, *Compt. rend.*, **155**, 721 (1912), *C.A.* **7**, 313.

[3] *Idem*, *Bull. soc. ch.*, [4] **9**, 542 (1911), *C.A.* **5**, 2792.

[4] Guareschi, *Z. anal. Ch.*, **52**, 545 (1913); cf. *C.A.* **7**, 3286.

[5] Giauque and Wiebe, *J. Am. Ch. Soc.*, **50**, 2198 (1928).

[6] Moles, *J. ch. phys.*, **19**, 135 (1921).

[7] Cf. U. S. Pat. 1,398,596. Others are listed in Gmelin, 8th ed., No. 7, p. 183.

of H_2, e.g., Pb, Sn, Fe, Al, Co, Ni, Zn and the metals of Groups V and VI. It unites with many oxides and hydroxides to produce bromides without change of valence: $PbO + 2\ HBr = PbBr_2 + H_2O$. If, however, the valence of the metal in the oxide or hydroxide is such that no corresponding bromide can be formed then reduction takes place as follows:

1. *Pb*, *Co*, *Ni* and *Mn* with valence greater than two become bivalent, e.g., $PbO_2 + 4\ HBr = PbBr_2 + Br_2 + 2\ H_2O$. Potassium permanganate liberates all the bromine from a bromide in presence of $CuSO_4$ (a separation of Br^- from Cl^-).[1]
2. As^{+5} forms As^{+3} and Br_2. The HBr must be concentrated and in excess, and the arsenic compound merely moistened with water: $H_3AsO_4 + 2\ HBr = H_3AsO_3 + Br_2 + H_2O$. In the presence of much water the reverse action takes place.
3. Sb^{+5} yields Sb^{+3} and Br_2.
4. Bi^{+5} forms Bi^{+3} and Br_2.
5. Fe^{+6} becomes Fe^{+3}, not Fe^{++}.
6. Cr^{+6} becomes Cr^{+3} (separation from Cl^- if the solution is sufficiently dilute). This reaction is largely dependent upon the concentration of H^+. Sulfates also exercise an important influence.[2]

Silver ion, Ag^+, precipitates Br^- as pale yellow silver bromide, AgBr, changing rapidly to a dark gray upon exposure to light. The product is insoluble in, and not decomposed by, HNO_3, soluble in concentrated NH_4OH, nearly insoluble in concentrated $(NH_4)_2CO_3$, slightly soluble in excess of Br^-, soluble in solutions of CN^- and $S_2O_3^{--}$. It is slowly decomposed by Cl_2.

Solutions of Hg_2^{++} precipitate mercurous bromide, Hg_2Br_2, pale yellow, soluble in excess of Br^-.

Lead, Pb^{++}, precipitates, from solutions not too dilute, lead bromide, $PbBr_2$, white, appreciably soluble in excess Br^-.

B. **With non-metals and their compounds.**

1. *Ferricyanides* in the presence of a small amount of water are reduced to $Fe(CN)_6^{-4}$. The HBr must be concentrated and in excess, also the ferricyanide should be merely moistened with H_2O, as in the presence of much water the reverse action takes place.
2. HNO_2 in dilute solution has no action on Br^- (distinction from I^-). HNO_3 forms NO and Br_2: $2\ HNO_3 + 6\ HBr = 2\ NO + 3\ Br_2 + 4\ H_2O$.
3. *Phosphorus* compounds are not reduced.
4. H_2SO_4 forms SO_2 and Br_2. Both acids must be concentrated and hot, otherwise the reverse action takes place. *Persulfates* react with Br^- in warm acid solution to form Br_2 (separation from Cl^-).
5. *Chlorine* liberates bromine from all bromides, even fused AgBr.

[1] Cf. Curtman and Leikind, *Ch. News*, **140**, 337–40 (1930).

[2] Bobtelsky and Rosenberg, *Z. anorg. allgem. Ch.*, **177**, 137 (1929), *C.A.* **23**, 2638.

$HClO_3$ becomes HCl. If the chlorate is concentrated other products may appear.

$HClO_4$ at room temperature does not liberate Br_2 from bromides. The presence of a small amount of Ru^{+3} causes the reaction to progress rapidly and smoothly: $8\ HBr + HClO_4 = 4\ Br_2 + HCl + 4\ H_2O$.[1]

6. *$HBrO_3$* reacts with HBr to form Br_2.
7. *HIO_3* forms I_2 and Br_2. The reaction is slow at room temperature.
8. *H_2O_2* liberates Br_2 from HBr at 100° (distinction from Cl^-).

7. Ignition. — Some bromides can be sublimed undecomposed in the presence of air; e.g., $AsBr_3$, $SbBr_3$, Hg_2Br_2 and $HgBr_2$. Some can be sublimed only in the absence of air and moisture; e.g., $AlBr_3$ and $NiBr_2$. Bromides of Na and K are not changed by heat. AgBr melts undecomposed. Many bromides, however, are more or less decomposed when ignited in the presence of air and moisture: $CuBr_2$ becomes Cu_2Br_2 and Br_2.

8. Detection. — Bromides are usually oxidized to Br_2 which is detected as indicated in §251, 8. The oxidizing agent used to liberate the bromine varies according to the conditions. Chlorine or persulfate is commonly employed, the former in cold, the latter in hot, solution. The bromine liberated may be extracted with CCl_4 which becomes light brown to a dark red brown depending upon the amount of Br_2. Other methods involve reaction of the bromine with (*a*) fluorescein to form the red eosin;[2] (*b*) fuchsin;[3] (*c*) Schiff's reagent for aldehydes.[4] A delicate test for Br^- involves first reaction with $K_2Cr_2O_7$ in H_2SO_4 solution. The Br_2 is absorbed in chloroform which is removed and washed two or three times with H_2O. Finally a small amount of KI solution is added. Upon shaking to produce a more intimate mixture free iodine is liberated by the Br_2 which colors the $CHCl_3$ purple.[5]

9. Determination. — (*a*) A bromide may be precipitated as AgBr, dried and weighed as such. (*b*) The solution containing Br^- may be treated with an excess of standard $AgNO_3$ and the excess determined by Volhard's method. (*c*) Br^- may be oxidized to Br_2 which is passed into a solution of KI. The I_2 is then titrated with $Na_2S_2O_3$. (Cf. §251, 9.)

§253. Bromic Acid. $HBrO_3$

1. Physical Properties. — The acid $HBrO_3$ is known only in solution. It is a colorless, odorless liquid and acts as a strong oxidizing agent. A solution of $HBrO_3$ is decomposed upon boiling, but by evaporation in a vacuum a solution containing about 50% of the acid may be obtained.

[1] Crowell, Yost and Carter, *J. Am. Ch. Soc.*, **51,** 786 (1929).

[2] Murmann, *Oesterr. Ch. Ztg.*, **32**, 36 (1929).

[3] Cf. Jones, Pharm. J., **106,** 475 (1921), *C.A.* **15,** 3956; Denigès and Chelle, *Ann. ch. anal. ch. appl.*, **23,** 81 (1918), *C.A.* **12,** 1373.

[4] Guareschi, *Giorn. farm. ch.*, **61,** 392 (1912), *C.A.* **7,** 35; cf. Casares and Tastet, *C.A.* **13,** 2321. The violet color is said to develop with as little as 0.0_32 g. of Br per liter present in the sample being tested.

[5] Jamieson, *J. Ch. Soc.*, (*Proc.*), **24,** 144 (1908).

2. Occurrence. — Neither the acid nor its salts are found in nature.

3. Preparation. — Bromates of the alkalis and alkaline earths may be obtained by treatment of their hydroxides with Br_2 at 100°: $6\ NaOH + 3\ Br_2 = 5\ NaBr + NaBrO_3 + 3\ H_2O$. The free acid is prepared by adding the calculated amount of dilute H_2SO_4 to $Ba(BrO_3)_2$.

5. Solubilities. — Silver bromate is soluble to the extent of about 0.2 g., barium bromate, about 0.7 g., thallous bromate, about 0.35 g., and lead bromate, about 1.35 g. per 100 cc. of H_2O at 20°. With the exception of some basic bromates, all others are soluble in water.

6. Reactions. — *A*. **With metals and their compounds.** — Bromic acid is a powerful oxidant. It is usually reduced to a bromide, sometimes only to Br_2. Its action on the free metals resembles that of $HClO_3$, with certain important differences. $HBrO_3$ yields H_2 only with Al, Mg and Na; while $HClO_3$ gives no free Cl_2, $HBrO_3$ yields Br_2 with most of the metals, the full equivalent being evolved with Zn, Cd, Cu, Fe and Sn.[1] Lower valences of the various metals as Hg_2^{++}, As^{+3}, Sb^{+3}, Sn^{++}, Cu_2^{++}, Fe^{++}, Mn^{++} and Cr^{+3}, are all oxidized to the higher form Hg^{++}, As^{+5}, Sb^{+5}, Sn^{+4}, Cu^{++}, Fe^{+3}, MnO_2 and CrO_4^{--}, respectively.[2]

Silver ion precipitates BrO_3^- as silver bromate, $AgBrO_3$, white, soluble in NH_4OH, easily soluble in HNO_3.[3] It is decomposed by HCl with evolution of Br_2 (distinction from AgBr).

B. **With non-metals and their compounds.**

1. $H_2C_2O_4$ forms CO_2 and Br_2. An excess of hot oxalic acid yields a bromide instead of free bromine.

HCNS becomes H_2SO_4.

$H_4Fe(CN)_6$ gives $H_3Fe(CN)_6$ and HBr. An excess of $HBrO_3$ carries the oxidation further.

2. HNO_2 reduces BrO_3^-, forming HNO_3 and Br_2:

$$HBrO_3 + 3\ HNO_2 = 3\ HNO_3 + HBr$$

3. *Phosphorus* in its lower valences becomes PO_4^{-3}, the BrO_3^- forming Br^-.

4. *Sulfur* and *sulfites* are oxidized to SO_4^{--} with formation of Br^-. Sulfides form S° first, then SO_4^{--}. *Thiosulfates* are changed to tetrathionates. The course of the reaction depends, however, on the acidity, temperature, etc.:

$$HBrO_3 + 6\ H_2S_2O_3 = 3\ H_2S_4O_6 + HBr + 3\ H_2O$$ [4]

[1] Hendrixson, *Proc. Iowa Acad. Sci.*, **3**, 179 (1907).
[2] Cf. Smith, *J. Am. Ch. Soc.*, **45**, 1116, 1420 (1923).
[3] Cf. Chamot and Mason, *Mikrochemie*, **5**, 97, 100 (1927).
[4] Fichter and Tschudin, *Helv. Ch. Acta*, **10**, 273 (1927).

5. *HCl* forms Cl_2 and Br_2.[1]
6. *HBr* reacts to produce Br_2.
7. *HI* yields I_2 and Br_2 except that with an excess of $HBrO_3$ the products are HIO_3 and Br_2.

7. Ignition. — All bromates are decomposed upon heating. $KBrO_3$, $NaBrO_3$ and $Ca(BrO_3)_2$ evolve oxygen and leave the bromides. $Co(BrO_3)_2$, $Zn(BrO_3)_2$ and other bromates evolve O_2 and Br_2, leaving an oxide.

8. Detection. — Bromate, as $KBrO_3$, in concentration greater than 0.001 g./cc. can be detected by precipitation as $AgBrO_3$ (cf. 6). Mercurous mercury, Pb^{++} and Ba^{++} also give precipitates, but a greater concentration of BrO_3^- is required. Bromate may also be reduced to bromide (§252, 8), or free bromine (§251, 8), and detected as such. Oxalic acid in dilute solution is a suitable reagent for the latter reaction.

Sulfuric and nitric acids liberate bromic acid from metallic bromates, the $HBrO_3$ remaining for some time intact, and the solution colorless. The gradual decomposition of the $HBrO_3$ is first a resolution into HBr and O, and as fast as HBr is formed it acts with $HBrO_3$, so as to liberate the bromine of both acids. Now, if the solution contains bromide as well as bromate, an abundance of free bromine is obtained immediately upon the addition of dilute sulfuric acid in the cold. Hence, if dilute sulfuric acid in the dilute cold solution does not color the carbon disulfide, and if the addition of solution of pure potassium bromide immediately develops the yellow color, while it is found that no other oxidizing agent is present, we have corroborative evidence of the presence of a bromate. And, if we treat a solution known to contain bromide with dilute sulfuric acid and carbon disulfide, and obtain no color, we have conclusive evidence of the absence of bromates. Hydrochloric acid transposes bromates and quickly decomposes the bromic acid, liberating both bromine and chlorine.

A mixture of bromate and iodate, treated with hydrochloric acid, furnishes bromine without iodine, coloring carbon disulfide yellow.

The ignited residue of bromates, in all cases if the ignition be done with sodium carbonate, will give the tests for bromides.

9. Determination. — Bromates may be titrated directly with suitable reductants, the endpoint being determined electrometrically, or an excess of such reductants as AsO_3^{-3}, $Na_2S_2O_3$, Ti^{+3} and Fe^{++} may be added and the excess determined as usual. Bromates may be reduced to free bromine or bromides and determined as such (§251–2).

[1] Cf. Smith, *loc. cit.*

§254. Iodine (Gr. *iodes* = violet). I = 126.92. Atomic No. 53. Usual valence 1, 5 and 7. Discovered by Courtois in 1812.

1. Physical Properties. — Density, 4.913 at room temperature;[1] melting point, 113.9°;[2] boiling point, 184°;[3] critical temperature, 512°;[4] vapor pressure, 0.305 mm. of Hg at 25°.[5] At ordinary temperatures, iodine is a soft blue-black crystalline solid with a metallic luster. The thin crystals have a brownish-red appearance. Precipitated iodine is a dark brown powder. Liquid iodine is brown by reflected light, red by transmitted light. The vapor is violet and has a characteristic odor. Its molecular formula below 600° is I_2. At about 1500° dissociation is practically complete, the molecules consisting of single atoms. Solid iodine burns the skin, but an aqueous or alcoholic solution is a good antiseptic. Other uses for iodine are: as AgI in photography, in the synthesis of certain dyes and in the treatment of goitre.[6]

2. Occurrence.[7] — Iodine is found free in some mineral waters, as iodide and iodate in sea water, and in the ashes of sea plants (kelp). Small quantities occur in several minerals, especially Chile saltpeter, as iodate and periodate. During 1930 about 1650 tons of iodine were produced. Chile furnished approximately 80%; Java, 9% (from mineral waters); and Japan, 7% (from kelp). The balance, about 4%, came from France, Norway, Scotland, Germany and the United States. More recently Russia has entered the field, but data are not available concerning either her actual or potential output. The price of iodine is normally \$4–\$5 per pound. It bears no relation to the cost of production, however, because there is no competition in the industry.

3. Preparation. — Practically all of the iodine marketed is sold as the element. It is a by-product of the manufacture of Chile saltpeter. (*a*) The "caliche" is digested with hot water. When saturated, the solution is allowed to cool, whereupon various salts — NaCl, K_2SO_4 and $MgSO_4$ — separate and are removed. Leaching with the mother liquor is repeated until the iodine content becomes 6–12 grams per liter. Then $NaHSO_3$ is added, which reduces the iodate to iodine: $2\ NaIO_3 + 5\ NaHSO_3 = I_2 + 3\ NaHSO_4 + 2\ Na_2SO_4 + H_2O$. The solution is neutralized with Na_2CO_3 and compressed air blown through the system. The liberated iodine is collected and freed from impurities by sublimation. The entire process is crude and very wasteful. (*b*) Iodine in the mineral waters of Java is said to be removed as cuprous iodide. (*c*) Iodine from kelp is obtained by first drying and burning the seaweed. The ashes are leached and, from the solution, K_2SO_4, KCl and NaCl are removed by crystallization. The filtrate is evaporated and the residue treated with H_2SO_4 and MnO_2 or with Cl_2. The liberated iodine is collected and purified.[8]

4. Oxides and Acids. — The oxides IO_2,[9] or I_2O_4, and I_2O_5[10] are well known. I_2O_3 has been reported but there is apparently some doubt about its composition, etc. The same is true of the heptoxide, I_2O_7. The well-known acids of iodine are hydriodic, HI; hypoiodous, HIO; iodic, HIO_3; and periodic, $HIO_4{\cdot}2H_2O$, or more accurately, H_5IO_6. The first and last two acids will be discussed in subsequent sections.

Hypoiodous acid, HIO, is very unstable. It quickly decomposes into I^- and IO_3^-

[1] Harris, *et al.*, *J. Am. Ch. Soc.*, **50**, 1599 (1928).
[2] Longinescu, *J. ch. phys.*, **25**, 72 (1928).
[3] Ramsey and Young, *J. Ch. Soc.*, **49**, 453 (1886).
[4] Syrkin, *Z. physik. Ch.*, *B*, **5**, 158 (1929).
[5] Baxter, *et al.*, *J. Am. Ch. Soc.*, **29**, 127 (1907).
[6] Careful investigation has shown that iodine, as usually administered in table salt and public supplies of drinking water, probably has no therapeutic effect.
[7] Cf. Roman, *Naturwissenschaften*, **18**, 792 (1930).
[8] Cf. Gmelin, 8th ed., No. 8, Pt. 1, p. 47 *et seq.*
[9] Muir, *J. Ch. Soc.*, **95**, 656 (1909).
[10] Lamb, *et al.*, *J. Am. Ch. Soc.*, **42**, 1636 (1920).

hence its preparation by interaction of a fixed alkali hydroxide and I_2 or the electrolysis of an iodide solution does not yield a very large amount of hypoiodite.[1]

5. Solubility. — The solubility of iodine in water at 20° is 0.029 g./100 cc.[2] It differs from Cl_2 and Br_2 in that it forms no hydrate. The solution slowly bleaches litmus, stains the skin brown and gradually decomposes in sunlight with formation of HI. Iodine is much more soluble in solutions of iodides than in pure water, due to the formation of a polyiodide, e.g., KI_3.[3] Iodine dissolves in many organic solvents: chloroform, 2.63 g. of iodine per 100 g. of $CHCl_3$ at 20°; carbon tetrachloride, approximately the same; ethyl alcohol, 26.6 g./100 g. of C_2H_5OH at 24.5°; benzene, 14.1 g./100 g. of C_6H_6 at 25°; etc. In general, solvents containing oxygen, as H_2O, C_2H_5OH, etc., dissolve iodine to form a brown solution, while non-oxygen compounds, CCl_4, $CHCl_3$, CS_2, etc., form violet solutions. This is not strictly true in all cases.[4, 5]

6. Reactions. — *A.* **With metals and their compounds.** — Warm iodine unites slowly with Pb° and Ag°; more rapidly with the elements Hg, As, Sb, Sn, Bi, Cu, Cd, Al, Fe, Cr, Co, Ni, Mn, Zn, Ba, Sr, Ca, Mg, K and Na. When used to oxidize metal ions, iodine invariably becomes I^-. It may, however, act with certain substances as a reductant, becoming oxidized to IO_3^- or IO_4^-. In acid or alkaline solution, the following are oxidized: Hg_2^{++} to Hg^{++}, Sn^{++} to Sn^{+4}; in an alkaline medium only, As^{+3} to As^{+5}, Sb^{+3} to Sb^{+5}, Cr^{+3} to Cr^{+6}, Fe^{++} to Fe^{+3}, Co^{++} to Co^{+3}, Mn^{++} to Mn^{+4}.

B. **With non-metals and their compounds.**

1. *Ferrocyanides* are oxidized to ferricyanides. The action, however, is slow and incomplete.
2. *HNO_3* forms HIO_3 and NO. Concentrated HNO_3 must be used. Action is slow. This is a good method for making HIO_3.
3. *H_3PO_2* and *H_3PO_3* are oxidized to H_3PO_4.
4. *H_2S* forms S and HI (separation of H_2S from AsH_3). The reaction does not take place in the absence of moisture. Under certain conditions, some of the S^{--} is oxidized to SO_4^{--}.

H_2SO_3 yields H_2SO_4.

[1] Skrabal and Buchta, *Ch. Ztg.*, **33**, 1184, 1193 (1909), *C.A.* **4**, 552, have considered the nature and behavior of HIO.

[2] Fedotieff, *Z. anorg. allgem. Ch.*, **69**, 28 (1910); Cf. Kracek, *J. Phys. Ch.*, **35**, 417 (1931), who gives values at other temperatures.

[3] For solubility in solutions of various halides, see: Carter and Hoskins, *J. Ch. Soc.*, **1929**, 580.

[4] Gmelin, 8th ed., No. 8, Pt. 1, p. 111–4, gives a list of solvents and the color of their iodine solutions.

[5] On the theory of the color of iodine solutions, see: Getman, *J. Am. Ch. Soc.*, **50**, 2883 (1928).

Thiosulfates produce tetrathionates: $2\ Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2\ NaI$.[1]

5. *Chlorine* reacts directly with iodine to form iodine chloride, ICl. If an excess of the reagent is present, ICl_3 is formed. In the presence of H_2O, HCl and HIO_3 are obtained: $5\ ICl + 3\ H_2O = 2\ I_2 + 5\ HCl + HIO_3$; in alkaline solution, Cl^- and IO_4^-: $I_2 + 7\ Cl_2 + 16\ NaOH = 14\ NaCl + 2\ NaIO_4 + 8\ H_2O$. Iodine chloride is also produced by the interaction of HIO and HCl. Due to this reaction, ICl is often a product of the reduction of IO_3^- or oxidation of I^- in concentrated HCl.

$HClO_3$ forms HIO_3 and HCl: $5\ HClO_3 + 3\ I_2 + 3\ H_2O = 6\ HIO_3 + 5\ HCl$.[2]

6. *Bromine* unites with I_2 to form iodine bromide, IBr, which is quickly decomposed by H_2O. In an alkaline system containing an excess of Br_2 a bromide and an iodate are formed:

$$I_2 + 5\ Br_2 + 12\ NaOH = 2\ NaIO_3 + 10\ NaBr + 6\ H_2O$$

Bromic acid is reduced to free bromine by I_2.

7. *Iodine* combines with soluble iodides to form a polyiodide, e.g., KI forms KI_3 (KII_2).

7. **Ignition.** — Iodine sublimes slightly at room temperature. Above 45° it vaporizes readily. If the vapor is cooled quickly it condenses to form unstable monoclinic crystals which soon revert to the orthorhombic form.

8. **Detection.** — Iodine is readily detected by the color of its solutions, yellow in H_2O and violet in CCl_4. A very delicate test is based on the blue color formed with a cold solution of starch. This reaction will reveal 0.005 mg. of I_2 in 1 cc. of solution[3] and is made more sensitive by the presence of CNS^-.[4] The formation of a violet vapor when heated is also characteristic of iodine. The presence of tannin interferes with the usual tests for I_2 unless a drop of $FeCl_3$ is added.

9. **Determination.** — Iodine may be reduced to iodide, precipitated as AgI, dried and weighed as such. *Volumetrically,* it may be titrated directly with standardized $Na_2S_2O_3$, using starch as an indicator or where the solution is too deeply colored, CCl_4 may be employed. *Colorimetrically,* iodine dissolved in an organic solvent to obtain the violet color may be compared with a standard similarly treated.

§255. Hydriodic Acid. HI

1. **Physical Properties.** — Hydriodic acid is a colorless gas. When solidified it melts at − 51° and boils at − 35.5°. The critical temperature is 150°; the critical pressure (calc.), 71 atmospheres. Heated above 180°, HI commences to dissociate into

[1] Pickering, *J. Ch. Soc.*, **37**, 128 (1880).

[2] See, however, Bellucci, *Gazz. ch. ital.*, **49**, II, 180 (1919), who believes the reaction distinctly more complicated.

[3] Turner, *J. Am. Ch. Soc.*, **52**, 2768 (1930); cf. Gmelin, 8th ed., No. 8, Pt. 1, p. 206.

[4] Ernst, *Bioch. J.*, **232**, 346 (1931), *C.A.* **25**, 2937.

H_2 and I_2, but at 1000° it has progressed to the extent of 29%. Its aqueous solution forms a constant boiling mixture at 127°, containing 57% HI and having a density of 1.708. Systems of higher density fume on exposure to air.

2. Occurrence. — Hydrogen iodide is not found free in nature but other iodides are widely distributed in small amounts. Chile saltpeter is an important source (cf. §254).

3. Preparation. — (*a*) Finely divided iodine is suspended in H_2O, then H_2S is passed into the mixture. More iodine is added as soon as the color disappears. $I_2 + H_2S = 2\,HI + S$. This method is satisfactory for a dilute solution only. (*b*) An iodide is heated with H_3PO_4[1] and the HI evolved absorbed in cold H_2O. (*c*) A suspension of iodine in water may be treated with a reductant as SO_3^{--}, Sn^{++}, AsO_3^{-3}, P°: $Na_2SO_3 + H_2O + I_2 = Na_2SO_4 + 2\,HI$; $2\,P + 5\,I_2 + 8\,H_2O = 2\,H_3PO_4 + 10\,HI$. Iodides of the alkalis are often obtained by first preparing ferrous iodide: $Fe + I_2 = FeI_2$; then treating the product with the carbonate of the desired alkali: $FeI_2 + Na_2CO_3 = FeCO_3 + 2\,NaI$.

5. Solubilities. — Hydriodic acid is readily soluble in water with which it forms three hydrates: $HI \cdot 2H_2O$, $HI \cdot 3H_2O$ and $HI \cdot 4H_2O$. All of these compounds melt between − 50° and − 30°.

The iodides of Pb, Ag, Hg, Cu_2^{++}, Pd^{++} and Tl^{+} are insoluble in water. Iodides of the other ordinary metals are soluble, those of Bi, Sn and Sb requiring a little free acid to hold them in solution. Lead iodide is slightly soluble in hot water, crystallizing out in golden yellow plates as the system cools. Mercuric iodide is readily soluble in excess of KI to form K_2HgI_4. Many of the other iodides are more soluble in KI than in pure H_2O. The iodides of Ba, Ca and Hg^{++} are soluble in alcohol; Hg_2I_2 and AgI are insoluble. All iodides in solution are transposed by HCl or by dilute H_2SO_4. Silver iodide is practically insoluble in NH_4OH or $(NH_4)_2CO_3$ (distinction from AgCl and approximately from AgBr), soluble in KCN. AgI and PbI_2 are soluble by decomposition in a solution of alkali thiosulfate: $AgI + Na_2S_2O_3 = NaI + NaAgS_2O_3$. Lead iodide is soluble in a solution of the fixed alkalis.

6. Reactions. — *A*. **With metals and their compounds.** — Ag^{+} precipitates I^{-} as silver iodide, AgI, pale yellow. The product blackens in the light without appreciable separation of iodine and becomes practically white when treated with NH_4OH. In the latter case washing with water restores the original color.

Solutions of Hg_2^{++} precipitate I^{-} as mercurous iodide, Hg_2I_2, yellow to green. Hg^{++} reacts with I^{-} to form first a yellow HgI_2, which quickly changes to the red form. The precipitate dissolves on stirring, until equivalent amounts are present, when the color deepens.

If Pb^{++} is added to a cold, not too dilute, solution of I^{-}, lead iodide, PbI_2, bright yellow, precipitates. It is appreciably soluble in excess of I^{-} and in hot water.

Palladous chloride, $PdCl_2$, precipitates I^{-} as black palladous iodide, PdI_2, insoluble in water, alcohol or dilute acids (distinction from Br^{-}). Palladous iodide is slightly soluble in excess of the alkali iodides, soluble in NH_4OH.

[1] **Sulfuric acid should not be used. See 6.**

If Cu^{++} is added to I^-, a precipitate of white cuprous iodide mixed with iodine is obtained: $2\,CuSO_4 + 4\,KI = Cu_2I_2 + 2\,K_2SO_4 + I_2$. If sufficient reductant, e.g., H_2SO_3, is present to reduce the liberated iodine to I^-, only the white cuprous iodide will be precipitated (distinction from Br^- and Cl^-).

When a solution of thallous ions, Tl^+, is added to I^-, a yellow precipitate of thallous iodide, TlI, is obtained.

When metals are attacked by HI an iodide is formed and H_2 is evolved. HI reacts with all metallic oxides, carbonates and hydroxides (except ignited Cr_2O_3) to form iodides. Frequently, however, iodine is liberated and an iodide of lower metallic valence is formed.

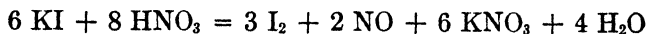
1. Pb having a higher valence becomes Pb^{++}.
2. As^{+5} becomes As^{+3}, but I^- has no action upon normal K_3AsO_4.
3. Sb^{+5} changes to Sb^{+3}.
4. Bi^{+5} forms Bi^{+3}.
5. Fe^{+3} yields Fe^{++} and I_2 (distinction from Br^- and Cl^-).
6. Cr^{+6} forms Cr^{+3}. K_2CrO_4 is not reduced by KI even upon boiling the concentrated solution. $K_2Cr_2O_7$ reacts slowly with I^- in the cold to give I_2 and Cr^{+3}. When the system is hot, the I^- is completely converted to I_2 (separation from Br^- and Cl^-): $6\,KI + K_2Cr_2O_7 + 7\,H_2O = 2\,Cr(OH)_3 + 3\,I_2 + 8\,KOH$. When AgI is boiled with $K_2Cr_2O_7$ and H_2SO_4 no iodine is evolved; the chromium is reduced and the iodide becomes iodate: $K_2Cr_2O_7 + AgI + 5\,H_2SO_4 = 2\,KHSO_4 + Cr_2(SO_4)_3 + AgIO_3 + 4\,H_2O$.
7. Co^{+3} and Ni^{+4} are each reduced to the bivalent state.
8. Manganese of higher valence becomes Mn^{++}. When I^- is boiled with MnO_4^- the manganese forms MnO_2 and the I^- is oxidized to IO_3^-: $6\,KMnO_4 + 3\,KI + 3\,H_2O = 3\,KIO_3 + 6\,MnO_2 + 6\,KOH$ (distinction from Br^-). $KMnO_4$ oxidizes HI to HIO_4 at ordinary temperatures in a solution containing a moderate excess of H_2SO_4.[1]

B. **With non-metals and their compounds.**

1. *$H_3Fe(CN)_6$* forms $H_4Fe(CN)_6$ and I_2; the reaction also takes place in neutral solution.
2. *HNO_2* yields NO and I_2 (separation of I^- from Cl^- and Br^-).

HNO_3 becomes NO and the I_2 liberated is oxidized to IO_3^- if the acid is concentrated:

$$6\,KI + 8\,HNO_3 = 3\,I_2 + 2\,NO + 6\,KNO_3 + 4\,H_2O$$

$$3\,I_2 + 10\,HNO_3 = 6\,HIO_3 + 10\,NO + 2\,H_2O$$

HNO_2 reacts more rapidly than HNO_3.

3. There is no reaction with *phosphorus.*

[1] Lang, *Z. anorg. allgem. Ch.*, **130**, 141 (1923).

4. Dilute H_2SO_4 has no action. Hot concentrated H_2SO_4 decomposes all iodides, those of Pb, Ag and Hg slowly but completely, SO_2 and I_2 being formed. $2\ NaI + 2\ H_2SO_4 = I_2 + SO_2 + Na_2SO_4 + 2\ H_2O$. If the iodide is added in excess to boiling H_2SO_4, the latter is reduced to a sulfide: $8\ KI + 9\ H_2SO_4 = 4\ I_2 + H_2S + 8\ KHSO_4 + 4\ H_2O$. Ammonium persulfate liberates iodine from dilute, acid solutions of I^- at ordinary temperatures; more rapidly upon boiling.[1]

5. *Chlorine* in excess forms HCl and HIO_3; with excess of iodide, HCl and I_2 are produced. In the presence of a fixed alkali, a periodate and a chloride are formed: $KI + 8\ KOH + 4\ Cl_2 = 8\ KCl + KIO_4 + 4\ H_2O$. *Hypochlorous* acid, HClO, oxidizes I^- to I_2, then to HIO_3 in acid solution; in alkaline solution a periodate is obtained.

$HClO_3$ added to an excess of HI gives HCl and I_2; with excess of $HClO_3$ the iodide goes to IO_3^-.

6. *Bromine* forms I_2 and HBr or a bromide.

$HBrO_3$ reacts with a large amount of HI to produce I_2 and HBr; with excess of $HBrO_3$ the iodine becomes iodate.

7. *Iodic acid* oxidizes an iodide to free iodine and is itself reduced to the same state: $HIO_3 + 5\ HI = 3\ I_2 + 3\ H_2O$. Periodic acid also oxidizes I^- to I_2.

8. *H_2O_2* changes I^- to I_2. Acids, Fe^{++}, Cu^{++} and other ions materially accelerate the reaction.

9. *Oxygen* reacts with HI to give I_2 and H_2O: $2\ HI + O_2 = I_2 + H_2O$. The reaction is markedly affected by traces of HNO_2. Among the iodides, some are affected by exposure to air, others, e.g., those of the alkalis, are not. Ozone promptly liberates I_2 from solutions of iodides.

7. Ignition. — As a general rule, iodides, strongly ignited in the presence of air and moisture, evolve iodine, leaving the oxide of the metal. Ignited in the absence of air or moisture, the following iodides are not decomposed: KI, NaI, BaI_2, CaI_2, SrI_2, MnI_2, AlI_3, SnI_4, PbI_2, AgI and HgI_2. Some iodides darken in color on heating: HgI_2 becomes dark red; TlI changes from yellow through orange to red; AgI also passes through the same color changes. If solid KI is fused with $KClO_3$, $KClO_4$ or $KBrO_3$, it is oxidized to KIO_3.

8. Detection. — The iodide is oxidized to free iodine by one of the reagents mentioned in (6) above. If a dry powder is to be tested, concentrated H_2SO_4 is usually employed, the iodine being detected by the violet fumes evolved, which condense on a cooler portion of the test tube. When a solution is to be tested, the usual reagent is persulfate or chlorine water. The iodine is recognized by the violet color when shaken with CCl_4. If only a small amount of I^- is present, chlorine must be added very cautiously or the I^- will be oxidized to IO_3^- and no purple color obtained. Where small amounts of I^- are sought, nitric acid is less liable to cause errors as

[1] For the velocity of this reaction, see: Jette and King, *J. Am. Ch. Soc.*, **51**, 1034 (1929).

relatively more HNO_3 is required to oxidize the I_2 to IO_3^-. The palladium iodide test is also very good for traces of I^-. The use of starch (cf. §254, 8) is also very satisfactory.[1]

If an insoluble iodide is encountered it may be treated with (a) H_2S, the insoluble sulfide removed by filtration, the excess of H_2S eliminated by boiling, and the solution tested for I^-; (b) Zn° and H_2SO_4: $2 AgI + Zn + H_2SO_4 = 2 Ag + ZnSO_4 + 2 HI$. The filtrate is tested for I^-. (c) A third method involves fusion of the insoluble iodide with Na_2CO_3, digestion of the melt with H_2O and, after filtration, addition of the oxidant to the acidified filtrate (if not acid I^- becomes IO_3^- or IO_4^-).[2]

9. Determination. — *Gravimetrically,* iodides may be determined (a) by precipitation as AgI, dried and weighed as such; (b) by precipitation as palladous iodide, PdI_2, which is dried and weighed or ignited to Pd and weighed. *Volumetrically,* iodides may be (a) oxidized to I_2 and titrated with $Na_2S_2O_3$;[3] (b) treated with an excess of standardized $AgNO_3$ and the excess titrated as in Volhard's method. The AgI need not be removed. The Fe^{+3} used as indicator should be added after the I^- has been precipitated.

§256. Iodic Acid. HIO_3

1. Physical Properties. — Iodic acid — usually the meta form, HIO_3, is indicated — is a white, crystalline solid, readily soluble in water (see 5 below). Its saturated aqueous solution at 18° has a density of 2.4711. It may be dehydrated at 110° to form iodic anhydride, I_2O_5 (see 4 below). Iodic acid forms a number of acid salts, the formulas for two of which may be written $MIO_3 \cdot HIO_3$, $MIO_3 \cdot 2HIO_3$. The iodates are less soluble and more stable than the corresponding chlorates or bromates.

2. Occurrence. — The free acid is not found in nature. The salt, $NaIO_3$, occurs in Chile saltpeter. Calcium iodate, $Ca(IO_3)_2$, also is found as a mineral. It has been reported as present in sea water.

The iodates are unimportant commercially. In analytical chemistry, KIO_3 and the mono-acid salt, $KIO_3 \cdot HIO_3$, are of particular interest because a large number of reductants change them quantitatively to I_2 in dilute acid solution and to ICl in concentrated HCl.

3. Preparation. — Iodic acid may be prepared by the action of powerful oxidants on iodine or iodides. Some of the reagents that have been suggested are HClO, $HClO_3$, HNO_3, H_2O_2, $H_2S_2O_8$, etc. (*a*) Possibly the most convenient method is to oxidize I_2 with a 24%–26% solution of $HClO_3$.[4] (*b*) H_2O_2 readily oxidizes I_2 in acid solution to HIO_3. (*c*) A very pure product may be obtained by treating I_2 with fuming HNO_3 and removing the excess acid by evaporation. The process is slow, expensive, and the yield low. (*d*) If I_2 is treated with an excess of Cl_2, iodic acid is formed: $I_2 + 5 Cl_2 + 6 H_2O = 2 HIO_3 + 10 HCl$. (*e*) Like the other halogenates, IO_3^- can be prepared by the electrolysis of an iodide in alkaline solution, using a cell without a diaphragm. (*f*) The action of I_2 on $AgNO_3$ forms HIO_3: $5 AgNO_3 + 3 I_2 + 3 H_2O = 5 AgI + 5 HNO_3 + HIO_3$.

[1] Kolthoff, *Pharm. Weekblad,* **56**, 391 (1919), *C.A.* **13**, 1434, has studied the influence of various factors on the sensitivity of this test. Cf. *Ibid.*, **62**, 1309 (1925), *C.A.* **20**, 723.

[2] For detection of iodides in presence of other halides, see, Gmelin, 8th ed., No. 8, Pt. 2, p. 209, *et seq.*

[3] The thiosulfate method for iodine, one of the most important in quantitative analysis because of its wide applicability, was first published by Pasquier, *Ann. ch. phys.*, [2] **73**, 310 (1840).

[4] Lamb, *et al.*, *J. Am. Ch. Soc.*, **42**, 1636 (1920).

Iodates of the alkalis and alkaline earths are easily made by the action of iodine on the hydroxides, the separation from any iodide formed being effected through fractional crystallization. The very stable potassium bi-iodate, $KIO_3 \cdot HIO_3$, is obtained by evaporating an aqueous solution containing equal quantities of KIO_3 and HIO_3.

4. Oxide. — If slowly heated to 110° and kept at that temperature for some time, HIO_3 gradually loses H_2O and becomes white di-iodine pentoxide, I_2O_5.[1] It is stable up to about 300°, decomposes into I_2 and O_2 upon exposure to light, reverts to HIO_3 on contact with H_2O, and is a strong oxidant. Its density at 25° is 4.799.[2] At 13° it dissolves in water to the extent of 187 g./100 cc. of H_2O. It is used chiefly to detect and determine carbon monoxide: $I_2O_5 + 5\ CO = 5\ CO_2 + I_2$. One part of CO in 30,000 of air is readily revealed by this means.

5. Solubilities. — Iodic acid is readily soluble in water, slightly over 233 g. dissolving in 100 cc. of H_2O at 20°. In such a solution the HIO_3 is apparently polymerized to $(HIO_3)_2$ or $H_2I_2O_6$. Upon dilution the simpler meta acid predominates.

In general, the iodates of the common metals are less soluble than the corresponding chlorates or bromates. The following example will give some idea of the range of solubility of the iodates. The temperature in all cases is practically 20° except for $Pb(IO_3)_2$, which is 25°, and the volume of solvent is consistently 100 cc.: $Pb(IO_3)_2$, 0.003 g.; $AgIO_3$, 0.006 g.; $Ba(IO_3)_2$, 0.022 g.; $TlIO_3$, 0.058 g.; $Ca(IO_3)_2$, 0.37 g.; KIO_3, 8.13 g.; $NaIO_3$, 9.0 g. All iodates are soluble in the fixed alkali hydroxides in so far as the corresponding metallic hydroxides are soluble in those reagents. A majority of the iodates are insoluble in alcohol.

6. Reactions. — *A*. **With metals and their compounds.** — A few metals are attacked evolving H_2 and leaving the metal iodate in solution, sometimes with traces of iodide. Some metal ions are oxidized, e.g., As^{+3} to As^{+5}, AsH_3 in excess to As°, but with the oxidant in excess AsO_4^{-3} is obtained; Sb^{+3} becomes Sb^{+5} but SbH_3 forms Sb°; Sn^{++} to Sn^{+4}; Cu_2^{++} to Cu^{++};[3] Fe^{++} to Fe^{+3}; etc.

A solution of Ag^+ precipitates IO_3^- as silver iodate, $AgIO_3$, white, crystalline, soluble in NH_4OH, in excess of hot HNO_3 and in HIO_3.

Ba^{++} precipitates IO_3^- as barium iodate, $Ba(IO_3)_2$, slightly soluble in cold, more soluble in hot water, insoluble in alcohol, soluble in hot, dilute HNO_3, readily soluble in cold dilute HCl. Dilute solutions of HIO_3 should be neutralized before testing with Ba^{++}. The compound, $Ba(IO_3)_2$, is readily separated from iodides by extraction of the latter with alcohol. When well washed, treated with a little H_2SO_3 and found to color CCl_4 violet, its evidence for IO_3^- is conclusive. Barium iodate is converted to $BaCO_3$ by $(NH_4)_2CO_3$. The precipitation of IO_3^- by means of Ba^{++} effects a separation from ClO_3^- and BrO_3^-.

[1] Baxter and Tilley, *J. Am. Ch. Soc.*, **31**, 201 (1909). Cf. Moles and Perez-Vitoria, *Z. physik. Ch.*, Bodenstein Festband, **1931**, 583, who state that iodic acid forms HI_3O_8 at 70° and I_2O_5 at 200°.

[2] Baxter and Tilley, *loc. cit.*

[3] If the Cu_2^{++} is in excess, the I^- formed gives Cu_2I_2 (distinction from ClO_3^- and BrO_3^-).

Pb^{++} gives, with IO_3^-, a white precipitate of $Pb(IO_3)_2$. Mercurous mercury gives a pale yellow precipitate, insoluble in dilute HNO_3 but soluble in HIO_3. Mercuric mercury also gives a precipitate with IO_3^- (distinction from ClO_3^- and BrO_3^-). Ferric ion gives, in solutions sufficiently concentrated, a pale yellow precipitate of $Fe(IO_3)_3$, slightly soluble in H_2O, readily soluble in excess of the reagent.

B. **With non-metals and their compounds.**

1. $H_2C_2O_4$ forms CO_2 and I_2. Action is slow unless the solution is hot.[1] Carbon (except diamond) heated in sealed tubes with HIO_3 becomes CO_2 and I_2 is the reduction product.

$H_4Fe(CN)_6$ yields $H_3Fe(CN)_6$ and I_2.

HCNS changes to H_2SO_4 and other products.

2. HNO_2 changes to HNO_3 with liberation of I_2.

3. PH_3, H_3PO_2, and H_3PO_3 form H_3PO_4 and I_2. With an excess of either reductant, I^- is obtained.

4. H_2S becomes S: $2\ HIO_3 + 5\ H_2S = I_2 + 5\ S + 6\ H_2O$. Other products as HI and H_2SO_4 may be obtained under suitable conditions.

Thiosulfates form first I_2 then an iodide.

Sulfurous acid reacts with HIO_3 to form ultimately H_2SO_4 and I_2: $2\ HIO_3 + 5\ H_2SO_3 = 5\ H_2SO_4 + I_2 + H_2O$. If an excess of sulfite is present, an iodide will be one of the final products. This combination is often used as a "clock" reaction.

5. *HCl*, if concentrated, produces ICl_3 and Cl_2, no iodine being liberated.

6. *HBr* forms Br_2 and I_2.

7. *HI* forms I_2 from both acids. The addition of tartaric acid to a mixture of KI and KIO_3 is sufficient to give an immediate test for I_2 with CCl_4. It must be noted, however, that an iodide alone, when acidified, will give a test for I_2 after a short time.

7. Ignition. — Potassium and sodium iodates on ignition form iodides with evolution of O_2. Many other iodates evolve O_2 but the iodide formed is further decomposed.

Iodates in a dry mixture with combustible bodies are reduced, on heating or concussion, with detonation, but much less violently than chlorates or nitrates.

8. Detection. — The iodate ion is usually detected by first removing any halide if necessary, then, after acidification, the IO_3^- is reduced to I_2 which is collected in CCl_4 or allowed to act on starch. The reductant often employed is H_2SO_3 because it acts rapidly in the cold, but traces of IO_3^- may escape detection for a slight excess of sulfite at once reduces the I_2 to I^- which does not affect the CCl_4. The following reductants have also been suggested: $H_4Fe(CN)_6$, H_3AsO_3, Cu_2Cl_2 and Fe^{++}. Iodate is

[1] Cf. Lemoine, *Compt. rend.*, **173**, 192 (1921), *C.A.* **15**, 3922, who has made a careful study of the reaction.

readily distinguished from the related ions ClO_3^- and BrO_3^- by the insolubility of its barium and lead salts.[1]

9. Determination. — Iodates may be precipitated as lead or silver iodate, dried and weighed. Volumetric methods are preferred, however, such as reduction with KI in acetic acid solution and titration of the I_2 with $Na_2S_2O_3$ (cf. §254). Reduction to the iodide may also be easily effected and the determination completed as indicated in §255.

§257. Periodic Acid. H_5IO_6

1. Physical Properties. — Some six or seven periodic acids, or their salts, have been reported but only four of the acids have been fairly well established: HIO_4, $H_4I_2O_9$, H_3IO_5 and H_5IO_6. The series may be considered as derived from the anhydride I_2O_7[2] by the addition of nH_2O where n may equal 1 to 7, i.e., HIO_4 is from $I_2O_7 \cdot H_2O$, $H_4I_2O_9$ from $I_2O_7 \cdot 2H_2O$, H_3IO_5 from $I_2O_7 \cdot 3H_2O$, etc.[3] Heating any of these polybasic acids yields HIO_4 which upon further dehydration becomes I_2O_5, O_2 and H_2O. Thus far the only periodic acid isolated in the free state is H_5IO_6. It forms colorless, monoclinic crystals which do not lose water at 100°. It melts slightly above 130°[4] and at 138° starts to decompose. Salts of this acid are the most common of the periodates and are apparently the most stable. In strong acid solution, periodic acids or their salts are very powerful oxidants and as such they are coming into more extensive use in analytical chemistry.

2. Occurrence. — Periodic acids are not found free in nature. Sodium periodate occurs in Chile saltpeter.

3. Preparation. — Free periodic acid is prepared by oxidizing I_2 with perchloric acid: $2\ HClO_4 + I_2 + 4\ H_2O = 2\ H_5IO_6 + Cl_2$. Other methods have been recommended but in general the objective is a salt and not the free acid. The most satisfactory procedure involves the treatment of an iodate in fixed alkali solution with Cl_2 or a hypochlorite: $NaIO_3 + 3\ NaOH + Cl_2 = Na_2H_3IO_6$[5] $+ 2\ NaCl$. The sodium periodate, being fairly insoluble in the medium, separates as crystals easily removed by filtration. Periodates may also be prepared by electrolysis of an alkaline solution of sodium or potassium iodate. A low current density, cold electrolyte, and the presence of a small amount of chromate ion favor the reaction.

5. Solubilities. — Periodic acid, H_5IO_6, is very soluble in H_2O but most of the periodates are only slightly soluble. They are, however, readily soluble in dilute HNO_3. Potassium periodate has a solubility of 0.66 g./100 cc. of H_2O at 13° — the solution reacts acid. The solubility of the sodium periodates is distinctly lower.

6. Reactions. — Periodic acids and the periodates act as strong oxidants in acid solution and produce effects similar to those obtained with the iodates.[6] Unlike the chlorates and perchlorates, both IO_3^- and IO_4^- are

[1] For a criticism of the usual methods for IO_3^- and a procedure claimed to detect 20 parts of IO_3^- in one million of sample, see: Andrews, *J. Am. Ch. Soc.*, **31**, 1035 (1909).

[2] This oxide has not been isolated.

[3] Cf. Friend, VIII, 252, and Mellor, II, 386, for a discussion of the constitution of the periodic acids.

[4] Some authorities state that decomposition begins at 110°.

[5] Whether the product is $Na_2H_3IO_6$ or $Na_3H_2IO_6$ apparently depends upon conditions, e.g., temperature, etc.

[6] Cf. Vitali, *Giorn. farm. ch.*, **59**, 18 (1910).

reduced by the same reagents. In certain cases neither is affected. Concerning many of the salts, often insufficient evidence is available to determine whether a particular one is a hydrate of one acid or the acid salt of another. With the existing uncertainty concerning the acids themselves, the situation could hardly be otherwise.

Among the metals, Zn° and Fe° are readily attacked by periodic acid, Cu° forms an iodate, Hg°, Sn° and Pb° are but slightly affected. Pb^{++} forms a white precipitate when added to a solution of sodium periodate, slightly acidified with HNO_3. The product turns yellow when heated. Silver nitrate, added to a periodate solution, forms a precipitate the color and nature of which depend upon the condition of the solution. If there is no excess of HNO_3, then Ag_2HIO_5 is obtained; a slight excess of the acid results in the separation of dark red $Ag_2H_3IO_6$; more acid produces slate-colored $Ag_3H_2IO_6$; with a larger excess, the orange $AgIO_4$ precipitates. Boiling the silver periodates in water causes them to become dark red in color. The freshly prepared compounds are readily soluble in NH_4OH. Mercurous ions form a yellow precipitate with periodates. Mercuric nitrate is said to yield a red-orange precipitate of $Hg_4I_2O_{11}$. Cu_2^{++} and Fe^{++} are oxidized to Cu^{++} and Fe^{+3}, the latter forming an insoluble periodate in nitric acid solution. Mn^{++} is readily oxidized to MnO_4^- [1] in hot acid solution.

Among the non-metals, oxalic acid is converted to CO_2. H_3PO_2, P° and H_3PO_3 are oxidized to H_3PO_4. Hydrosulfic acid, H_2S, is immediately oxidized to S° or SO_4^{--}, depending upon conditions. Sulfurous acid becomes H_2SO_4. There is no separation of iodine if the reactants are present in equivalent amounts. An excess of sulfite will, of course, reduce the HIO_3 initially formed to I_2 then to HI. Hydrochloric acid first forms HIO_3 and Cl_2: $H_5IO_6 + 2\ HCl = HIO_3 + Cl_2 + 3\ H_2O$. Ultimately ICl_3 is obtained. Hydriodic acid first reduces periodates to IO_3^-. If an excess of the reductant is added, free iodine is formed, which combines with the I^- to give a polyiodide, I_3^-. Hydrogen peroxide reduces periodates to iodates with liberation of O_2. With H_5IO_6, tannin forms a flocculent precipitate (distinction from IO_3^-). The precipitate is soluble in NH_4OH and the solution becomes dark red on exposure to the air.

8. Detection. — Periodates may be detected by (*a*) their powerful oxidizing action, (*b*) reduction to I_2 which colors CCl_4 purple, (*c*) reduction to iodide which may be detected as indicated on p. 551. The reactions with Ag^+ and Hg_2^{++} are also characteristic.

9. Determination. — Periodates may be reduced to free iodine which is titrated with $Na_2S_2O_3$ (cf. §254), or to an iodide which is determined as described in §255.

[1] Willard and Greathouse, *J. Am. Ch. Soc.*, **39**, 2366 (1917), have employed this reaction for the quantitative oxidation of Mn.

ANALYSIS OF A SOLUTION FOR ACID RADICALS

SULFATE, SULFITE, CARBONATE, OXALATE, ARSENATE, PHOSPHATE, SULFIDE, IODIDE, BROMIDE, CHLORIDE, CHLORATE, NITRATE

§260. The following discussion applies to a solution containing no metals that will interfere with the reactions being employed for the identification of the acid radicals. Further, only a limited number of the more common radicals are being considered, so the procedures suggested are subject to modification if the list is made more extensive. It is felt, however, that the list covers the more important radicals, and is sufficiently extensive to provide practice in a reasonable variety of procedures, so that the principles involved and the precautions required may be made clear.

As explained in the introductory sections on the Theory of Group Separations (p. 83–7), while the same reactions are available for precipitation of the acid radicals as for precipitation of the metals, the former do not lend themselves readily to separation into a series of groups by means of selected group reagents. For this reason it becomes simpler to apply tests for these on separate portions of the original solution, than to try to fit them into a scheme of systematic separation into groups. For convenience in discussing these acid radicals, it is permissible to speak of them as found in Groups I, II and III, without implying that they are divided into groups by precipitation processes, and that the precipitates thus obtained are filtered out, washed, and then systematically examined for the various acid radicals present. Rather, the group tests are applied on separate portions of the original solution to eliminate individual testing for several acid radicals, all of which may be shown to be absent by such a preliminary test.

The three groups are differentiated by the use of (*a*) Ca^{++} and Ba^{++} in neutral or alkaline solution, and (*b*) Ag^{+} in 1.5–2 *N* HNO_3 solution. **Group I** consists of those acid radicals whose Ba and (or) Ca salts are insoluble in water. This includes the first six of the radicals listed above, namely, SO_4^{II}, SO_3^{II}, CO_3^{II}, $C_2O_4^{II}$, AsO_4^{III} and PO_4^{III}. **Group II** consists of those acid radicals whose Ag salts may be precipitated in a cold solution which is moderately acid with HNO_3. This includes the next four radicals, namely, S^{II}, I^{I}, Br^{I} and Cl^{I}. **Group III** consists of those acid radicals whose common salts are soluble, the last two in the list being included here; namely, ClO_3^{I} and NO_3^{I}.

In this discussion of the methods for detection of negative radicals, the phrase acid radical has been used rather than the word anion, to call attention to the fact that in aqueous solution the material being identified may not exist in an independent form. Only in the case of the strong acids may the acid radical be considered to occur as the simple ion, whether the

solution is alkaline or acid. Obviously, in the case of the weaker acids the concentration of the simple anion will be low in all but moderately alkaline solutions; while polybasic acids of considerable strength may yield chiefly intermediate ions. Using the data for the primary and secondary ionization constants for H_2SO_3, it is instructive to calculate the relative amounts of H_2SO_3, HSO_3^-, and SO_3^{--} that will be present in a sulfite solution at several different concentrations of hydrogen ion.

$$K_{H_2SO_3} = \frac{[H^+] \times [HSO_3^-]}{[H_2SO_3]} = 1.7 \times 10^{-2}$$

$$K_{HSO_3^-} = \frac{[H^+] \times [SO_3^{--}]}{[HSO_3^-]} = 5 \times 10^{-6}$$

From these the following ratios are obtained for varying concentrations of H^+:

$[H^+] =$	0.1	1×10^{-4}	1×10^{-7}	1×10^{-10}	1×10^{-14}
$\frac{[HSO_3^-]}{[H_2SO_3]} =$	0.17	170	1.7×10^5	1.7×10^8	1.7×10^{12}
$\frac{[SO_3^{--}]}{[HSO_3^-]} =$	5×10^{-5}	5×10^{-2}	50	5×10^4	5×10^8

According to these figures, in the presence of 0.1 N H^+ a sulfite solution will be approximately 85.5% H_2SO_3 and 14.5% HSO_3^-, the fraction as SO_3^{--} being practically negligible (7.2×10^{-4}%). In the presence of 1×10^{-4} N H^+, the composition shifts to 0.56% H_2SO_3, 94.7% HSO_3^-, and 4.73% SO_3^{--}. In neutral solution, the amount of H_2SO_3 becomes negligible, the solution being essentially 2% HSO_3^- and 98% SO_3^{--}.

With weaker acids it requires a more alkaline solution to cause the simple negative ion to predominate. Thus, with carbonic acid in neutral solution, the material is about 25% H_2CO_3 and 75% HCO_3^-, and at $[H^+] = 1 \times 10^{-10}$ N the material is only 37% CO_3^{--} and 63% HCO_3^-. In the case of phosphoric acid, when $[H^+] = 1 \times 10^{-13}$ N ($[OH^-] = 0.1$ N), the material is approximately 80% PO_4^{-3} and 20% HPO_4^{--}. With H_2S, the weakest acid in the list, in neutral solution the material is more than 50% H_2S; while in the presence of N OH^- it is about 10% S^{--} and 90% HS^-.

Clearly the methods of identification employed do not distinguish between cases of the above sort. It would be necessary to supplement the identification with a determination of the approximate acidity (or alkalinity) of the solution and use the ionization constants for the different acids, if one wished to show more accurately the ionic composition of the solution. The common cases are shown in Table 43.

TABLE 43

Ionic Characteristics of Some Acids

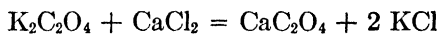
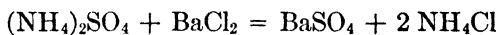
Acids	Ionization Constants	Ionization ratios at several acidities					
		Ratio	*p*H=1†	*p*H=4	*p*H=7	*p*H=10	*p*H=14
H_2SO_4	$\frac{[H^+]\times[HSO_4^-]}{[H_2SO_4]} = $ —*	$\frac{[HSO_4^-]}{[H_2SO_4]}$	—*				
HSO_4^-	$\frac{[H^+]\times[SO_4^{--}]}{[HSO_4^-]} = 3\times10^{-2}$	$\frac{[SO_4^{--}]}{[HSO_4^-]}$	0.3	300	3×10^5	3×10^8	3×10^{12}
H_2SO_3	$\frac{[H^+]\times[HSO_3^-]}{[H_2SO_3]} = 1.7\times10^{-2}$	$\frac{[HSO_3^-]}{[H_2SO_3]}$	0.17	170	1.7×10^5	1.7×10^8	1.7×10^{12}
HSO_3^-	$\frac{[H^+]\times[SO_3^{--}]}{[HSO_3^-]} = 5\times10^{-6}$	$\frac{[SO_3^{--}]}{[HSO_3^-]}$	5×10^{-5}	5×10^{-2}	50	5×10^4	5×10^8
H_2CO_3	$\frac{[H^+]\times[HCO_3^-]}{[H_2CO_3]} = 3\times10^{-7}$	$\frac{[HCO_3^-]}{[H_2CO_3]}$	3×10^{-6}	3×10^{-3}	3.0	3×10^3	3×10^7
HCO_3^-	$\frac{[H^+]\times[CO_3^{--}]}{[HCO_3^-]} = 6\times10^{-11}$	$\frac{[CO_3^{--}]}{[HCO_3^-]}$	6×10^{-10}	6×10^{-7}	6×10^{-4}	0.6	6×10^3
$H_2C_2O_4$	$\frac{[H^+]\times[HC_2O_4^-]}{[H_2C_2O_4]} = 3.8\times10^{-2}$	$\frac{[HC_2O_4^-]}{[H_2C_2O_4]}$	0 38	380	3.8×10^5	3.8×10^8	3.8×10^{12}
$HC_2O_4^-$	$\frac{[H^+]\times[C_2O_4^{--}]}{[HC_2O_4^-]} = 4.9\times10^{-5}$	$\frac{[C_2O_4^{--}]}{[HC_2O_4^-]}$	4.9×10^{-4}	0.49	4.9×10^2	4.9×10^5	4.9×10^9
H_3AsO_4	$\frac{[H^+]\times[H_2AsO_4^-]}{[H_3AsO_4]} = 5\times10^{-3}$	$\frac{[H_2AsO_4^-]}{[H_3AsO_4]}$	5×10^{-2}	50	5×10^4	5×10^7	5×10^{11}
$H_2AsO_4^-$	$\frac{[H^+]\times[HAsO_4^{--}]}{[H_2AsO_4^-]} = 4\times10^{-5}$	$\frac{[HAsO_4^{--}]}{[H_2AsO_4^-]}$	4×10^{-4}	0.4	400	4×10^5	4×10^9
$HAsO_4^{--}$	$\frac{[H^+]\times[AsO_4^{-3}]}{[HAsO_4^{--}]} = 6\times10^{-10}$	$\frac{[AsO_4^{-3}]}{[HAsO_4^{--}]}$	6×10^{-9}	6×10^{-6}	6×10^{-3}	6.0	6×10^4
H_3PO_4	$\frac{[H^+]\times[H_2PO_4^-]}{[H_3PO_4]} = 1.1\times10^{-2}$	$\frac{[H_2PO_4^-]}{[H_3PO_4]}$	0.11	1.1×10^2	1.1×10^5	1.1×10^8	1.1×10^{12}
$H_2PO_4^-$	$\frac{[H^+]\times[HPO_4^{--}]}{[H_2PO_4^-]} = 2\times10^{-7}$	$\frac{[HPO_4^{--}]}{[H_2PO_4^-]}$	2×10^{-6}	2×10^{-3}	2.0	2×10^3	2×10^7
HPO_4^{--}	$\frac{[H^+]\times[PO_4^{-3}]}{[HPO_4^{--}]} = 3.6\times10^{-13}$	$\frac{[PO_4^{-3}]}{[HPO_4^{--}]}$	3.6×10^{-12}	3.6×10^{-9}	3.6×10^{-6}	3.6×10^{-3}	36
H_2S	$\frac{[H^+]\times[HS^-]}{[H_2S]} = 9.1\times10^{-8}$	$\frac{[HS^-]}{[H_2S]}$	9.1×10^{-7}	9.1×10^{-4}	0.91	9.1×10^2	9.1×10^6
HS^-	$\frac{[H^+]\times[S^{--}]}{[HS^-]} = 1.2\times10^{-15}$	$\frac{[S^{--}]}{[HS^-]}$	1.2×10^{-14}	1.2×10^{-11}	1.2×10^{-8}	1.2×10^{-5}	0.12
HI	$\frac{[H^+]\times[I^-]}{[HI]} = $ —*	$\frac{[I^-]}{[HI]}$	—*				
HBr	$\frac{[H^+]\times[Br^-]}{[HBr]} = $ —*	$\frac{[Br^-]}{[HBr]}$	—*				
HCl	$\frac{[H^+]\times[Cl^-]}{[HCl]} = $ —*	$\frac{[Cl^-]}{[HCl]}$	—*				
$HClO_3$	$\frac{[H^+]\times[ClO_3^-]}{[HClO_3]} = $ —*	$\frac{[ClO_3^-]}{[HClO_3]}$	—*				
HNO_3	$\frac{[H^+]\times[NO_3^-]}{[HNO_3]} = $ —*	$\frac{[NO_3^-]}{[HNO_3]}$	—*				

* These are typical strong acids, highly ionized in the way shown in column 2.
† *p*H = 1, 4, etc., means $[H^+] = 1 \times 10^{-1}, 1 \times 10^{-4}$, etc.

PROCEDURE FOR THE ANALYSIS FOR GROUP I ACID RADICALS

§261. **Manipulation.** — Place 2–3 cc. of the original solution in a test tube. Test with litmus paper. If acid, neutralize with NH_4OH; if neutral or alkaline, use the solution without further treatment. Add 0.5 cc. each of $BaCl_2$ and $CaCl_2$. If a white precipitate forms, the presence of one or more acid radicals of Group I is shown.

$$(NH_4)_2SO_4 + BaCl_2 = \underline{BaSO_4} + 2\,NH_4Cl$$

$$K_2C_2O_4 + CaCl_2 = \underline{CaC_2O_4} + 2\,KCl$$

In this case, proceed with the individual tests for the Group I radicals (§§263–74). If no precipitate is obtained, Group I acid radicals may all be considered absent.

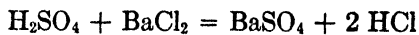
§262. **Notes.** — 1. If the original solution is acid it would be entirely feasible to have metals present in the solution such that the hydroxides would precipitate on neutralization with NH_4OH. Further, if Group I anions from the weaker acids were present along with various of the heavy metals, corresponding salts might precipitate as the solution is neutralized, thus causing the loss of such acid radicals if the precipitate were filtered out and discarded. For the present, it may be assumed that no such complications will be introduced in the preliminary study of the anions. If such a difficulty were encountered, it would be necessary either to carry out a preliminary treatment of the solution (such as boiling with concentrated Na_2CO_3 solution), that would separate the acid radicals from the interfering metals before trying the test for Group I acid radicals, or else to try the tests for the individual acid radicals without attempting to identify them as a group.

2. It is necessary to neutralize the original solution if acid, because many of the Ba and Ca salts fail to precipitate in acid solution. In fact, $BaSO_4$ is the only one that will precipitate at all readily in moderately acid solution. Others, such as $BaSO_3$ and CaC_2O_4, may be precipitated in slightly acid solution (as in the presence of $HC_2H_3O_2$), while others require a neutral or slightly alkaline solution for prompt precipitation.

3. Since only small portions of the original solution are being used for these preliminary tests, the procedure is somewhat less sensitive for small quantities of these acid radicals than it would be if larger portions were being tested. Quantities of the Group I acid radicals down to 1–2 mg. should be recognized, however, by the above procedure. If it is desired to identify these acid radicals in more dilute solutions than 0.5–1.0 mg. per cc., it may be necessary to use more of the original solution either for the preliminary group test or for the individual tests.

Test for Sulfate Radical

§263. **Manipulation.** — If the original solution is neutral or alkaline, acidify 2–3 cc. of the solution with 5 *N* HCl, adding about 1–2 cc. excess, then add 0.5 cc. of $BaCl_2$ solution. If SO_4^{--} is present a white, finely divided precipitate will form.

$$H_2SO_4 + BaCl_2 = \underline{BaSO_4} + 2\,HCl$$

Reserve the solution to test for sulfite radical (§265).

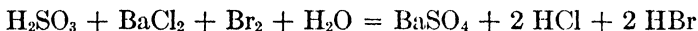
§264. **Notes.** — 1. If the solution contained Ag^+, the Cl^- added would cause the precipitation of white, curdy AgCl. This is sufficiently different in appearance from $BaSO_4$ so that there is little chance for confusion even if the $BaCl_2$ were added first and then HCl used to test the solubility of the precipitate in that reagent. If Ag^+ were present, it could be removed with excess HCl, the precipitate being discarded and the filtrate tested for SO_4^{--}. Or, HNO_3 and $Ba(NO_3)_2$ might be used in place of HCl and $BaCl_2$. With this second procedure care should be taken to use only moderate amounts of HNO_3 and of $Ba(NO_3)_2$, since the latter salt is only slightly soluble in strong HNO_3 and may be obtained occasionally as a precipitate that looks more or less like $BaSO_4$.

2. Of the other Group I anions, SO_3^{--} is most likely to precipitate and be mistaken for SO_4^{--}. With the moderately acid solution suggested above, however, and with $BaCl_2$ used cautiously, there is little danger of error from this source. As a matter of fact, sulfurous acid is oxidized so readily by atmospheric oxygen that one usually obtains a slight test for SO_4^{--} on most of the solutions containing SO_3^{--}, even though due care has been taken to prevent a direct interference with the test for SO_4^{--}.

3. The effect of the HCl (or HNO_3) in preventing the precipitation of $BaSO_3$ (BaC_2O_4, etc.) is due to H^+, which combines with the other anions of Group I to form slightly ionized substances (HSO_3^-, H_2SO_3, etc.), thus lowering the concentration of the simple anion to such an extent that insufficient Ba salt forms to precipitate.

Test for Sulfite Radical

§265. **Manipulation.** — If the test for SO_4^{--} was negative, add to the solution on which the test for SO_4^{--} was applied, about 5 cc. of bromine water,[1] warm, and look for a finely divided white precipitate of $BaSO_4$.

$$H_2SO_3 + BaCl_2 + Br_2 + H_2O = BaSO_4 + 2\,HCl + 2\,HBr$$

If the test for SO_4^{--} on the original solution was positive, add to the solution in which the test was obtained (§263) 1–2 cc. more of $BaCl_2$, shake, filter, and test the filtrate with a few drops of $BaCl_2$ for completeness of precipitation. When precipitation is complete, discard the precipitate and test the filtrate with bromine water as above.

§266. **Notes.** — 1. There is no direct precipitation reaction by which the sulfite radical may be identified, therefore it is necessary to convert it to some form for which a direct test may be applied. With strong reducing agents ($SnCl_2$ in HCl solution) it may be reduced to H_2S, and with strong oxidizing agents it is readily oxidized to SO_4^{--}. In either case it is necessary to take adequate steps to remove all of such product originally present in the solution before applying the test for SO_3^{--}.

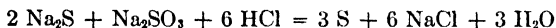
2. Barium sulfate usually precipitates in a very finely divided form, running through the ordinary "qualitative" filter paper to some extent. Usually refiltering, or the use of a filter paper of finer texture will take care of this. A coarser precipitate may be obtained by carrying out the precipitation slowly from a hot solution, but, in using such procedures, care should be taken to avoid extreme conditions that might result in loss of SO_2 by volatilization while the SO_4^{--} is being removed.

3. Certain oxidants, such as NO_3^-, may form a reasonably stable combination with SO_3^{--} so long as the solution is neutral or alkaline, but when HCl and $BaCl_2$ are added, there is danger of oxidation of the H_2SO_3 and precipitation as $BaSO_4$ during the operation that is aimed at removal of SO_4^{--} in order that the test for SO_3^{--} may be applied. Under such conditions it may be best to precipitate from neutral solution with excess $BaCl_2$, filter and wash (thus separating both sulfite and sulfate from any soluble oxidant

[1] This reagent may contain SO_4^{--} as an impurity.

such as NO_2^-), and then examine the precipitate for sulfite radical. This may be done either by digesting the precipitate for several minutes with 5 cc. of cold 2–3 *N* HCl, filtering, and treating with bromine water; or by boiling the precipitate for a few minutes with 5–10 cc. of 3 *N* Na_2CO_3, then filtering, acidifying the filtrate with HCl, precipitating SO_4^{--} with excess $BaCl_2$, discarding the precipitate, and treating the filtrate with Br_2-water, as usual.

4. Sulfide ion also interferes with the test for a sulfite. This interference may be of two sorts. If S^{--} is present, an apparent test for SO_3^{--} may be obtained, due to oxidation of S^{--} to SO_4^{--}. Or, if SO_3^{--} is also present, it will be reduced when the solution is acidified and may be filtered out as S°, along with the $BaSO_4$.

$$2\ Na_2S + Na_2SO_3 + 6\ HCl = 3\ S + 6\ NaCl + 3\ H_2O$$

Thus, to test for SO_3^{--} in a solution containing S^{--}, it becomes necessary to separate these from each other by precipitation reactions (as in note 2) in the original neutral or alkaline solution.

5. Another test for sulfite radical, depending on the weakness and instability of H_2SO_3, and the pronounced odor of SO_2, consists in acidifying the solution with H_2SO_4, warming, and noting the characteristic odor (of burning sulfur).

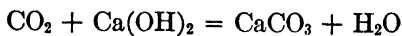
6. Since H_2SO_3 is a strong reductant, decolorizing dilute $KMnO_4$ solution rapidly in the cold, it is possible to apply another test as follows: Acidify a test portion of the original solution with dilute H_2SO_4, cool, and add a few drops of diluted $KMnO_4$ solution (1 part of the laboratory solution diluted with 10 parts of water). If the red permanganate color disappears quickly, a sulfite is probably present.

$$2\ KMnO_4 + 5\ H_2SO_3 = 2\ MnSO_4 + K_2SO_4 + 2\ H_2SO_4 + 3\ H_2O$$

The chief interference (among the acid radicals) with this test comes from S^{--} and I^-, or $C_2O_4^{--}$ if Mn^{++} is present. These interferences may be overcome by precipitation with excess $BaCl_2$ in neutral or alkaline solution, followed by thorough washing. The precipitate may then be placed in a beaker, treated with about 5 cc. of dilute H_2SO_4, and the permanganate test applied.

Test for Carbonate Radical

§267. **Manipulation.** — Place 2–3 cc. of the original solution in a test tube that is equipped with a one-hole rubber stopper and delivery tube. Add 3–5 cc. of $HC_2H_3O_2$ (sufficient to make distinctly acid), insert the rubber stopper and heat the test tube, bubbling the gas through several cc. of lime water, $Ca(OH)_2$, contained in a second test tube. A white precipitate indicates a carbonate.

$$Na_2CO_3 + 2\ HC_2H_3O_2 = CO_2 + 2\ NaC_2H_3O_2 + H_2O$$
$$CO_2 + Ca(OH)_2 = \underline{CaCO_3} + H_2O$$

§268. **Notes.** — 1. This test depends upon the weakness and instability of carbonic acid, and the readiness with which CO_2 may be driven out of the solution by heating. Sulfurous acid is also unstable, but it is a stronger acid than H_2CO_3, and SO_2 is much more soluble in water than CO_2. By using dilute $HC_2H_3O_2$, the interference of SO_2 may be avoided. If excess of HCl or H_2SO_4 were used instead of dilute $HC_2H_3O_2$, SO_2 might be given off in sufficient quantities to produce a white precipitate of $CaSO_3$, similar in appearance to $CaCO_3$, in the lime water.

2. The above test for CO_2 may be modified (and made somewhat less satisfactory), by acidifying a portion of the original solution and then holding in the space immediately above the solution a glass rod that has just been dipped into lime water. Any CO_2 given off reacts with the film of $Ca(OH)_2$ on the end of the rod, precipitating $CaCO_3$

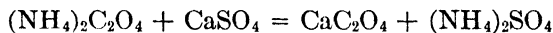
and causing the film to turn milky in appearance. Since the concentration of CO_2 in the air of the laboratory may be distinctly above normal, it is desirable to compare the result with a blank test to make sure that the milky effect is obtained more quickly when carbonate ion is present than from absorption of CO_2 from the air.

3. Since CO_2 is a normal constituent of the air (and in the laboratory its concentration is usually above normal, due to gas burners, etc.), any solution that has been exposed to the air will contain small amounts of CO_2. Even distilled water contains a perceptible quantity of CO_2, while an alkaline solution will absorb considerable CO_2 from the air. In case the test for carbonate is slight, it may be desirable to put a corresponding amount of distilled water and reagents through the same test to see if there is a significant difference.

4. Another test for CO_3^{--} that is frequently used is the *effervescence* test. This depends upon the fact that CO_2 is only slightly soluble in water, so if an aqueous solution containing a moderate amount of CO_3^{--} is acidified, more CO_2 may be formed than will remain in solution, the excess forming gas bubbles in the liquid, which rise to the surface and break. Since CO_2 is soluble in water at room temperature to the extent of about 15 mg. in 10 cc., and appreciable supersaturation effects are obtained, the test fails with the more dilute carbonate solutions. Further, this test is interfered with by sulfide ion, and by high concentration of sulfite ion when strongly acidified.

Test for Oxalate Radical

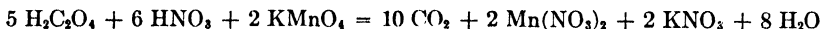
§269. **Manipulation.** — Place 2–3 cc. of the original solution in a test tube. If the solution is either acid or alkaline, neutralize it, add 2–3 cc. of $HC_2H_3O_2$, and then add 3–5 cc. of a saturated solution of $CaSO_4$ (or 2–3 cc. of 0.05 *N* $CaCl_2$). A finely divided white precipitate indicates the presence of an oxalate.

$$(NH_4)_2C_2O_4 + CaSO_4 = \underline{CaC_2O_4} + (NH_4)_2SO_4$$

§270. **Notes.** — 1. This test depends upon the fact that CaC_2O_4 is sufficiently insoluble to precipitate readily even with only a very small amount of Ca^{++} added (in contrast with $CaSO_4$ and $CaSO_3$). Further, $HC_2O_4^-$ is sufficiently ionized to supply oxalate ion effectively in spite of the presence of acetic acid (in contrast with $H_2PO_4^-$, HCO_3^- and $H_2AsO_4^-$, which do not supply HPO_4^{--}, CO_3^{--} or $HAsO_4^{--}$ in sufficient concentration for precipitation of the corresponding Ca salts).

2. In using $CaSO_4$ for this test, due account must be taken of the possible precipitation of an insoluble sulfate in the case of solutions that may contain the common metals as well as acid radicals. A dilute solution of $CaCl_2$ or $Ca(NO_3)_2$ may be used instead of $CaSO_4$ to avoid this difficulty. In substituting either of these reagents, it is important to use a sufficiently dilute solution to avoid possible precipitation of $CaSO_4$ or $CaSO_3$.

3. An alternative test for oxalate radical which is frequently used is the *decolorization test* (similar in principle to the test for SO_3^{--} in §266, note 5). A warm, nitric acid solution containing an oxalate reduces MnO_4^- readily. Since any other reductant will do the same thing, this effect can be used as a confirmatory test for $C_2O_4^{--}$ only after a series of operations adequate to separate $C_2O_4^{--}$ from other possible reductants. The steps necessary to accomplish this (in the absence of interfering metals) are as follows: Precipitate any $C_2O_4^{--}$ with excess of $CaCl_2$ in an acetic acid solution. Filter and wash thoroughly. (This separates $C_2O_4^{--}$ from the soluble reductants, such as I^-, Br^-, Cl^-, S^{--}, and most of the SO_3^{--}.) Transfer the precipitate to a casserole, add 5–10 cc. of 5 *N* HNO_3, heat to boiling and let boil gently (without much evaporation) for 2–3 minutes. (This serves to oxidize any H_2SO_3, and to decompose and remove any HNO_2, whether formed from oxidizing H_2SO_3 or present as decomposition product in the HNO_3 used.) Oxalic acid is a mild enough reductant to be only slightly oxidized by the HNO_3, providing the concentration of the latter and the length of time of boiling are reasonably controlled. Let the solution cool to about 60° (the casserole should still feel rather hot when rested on the palm of the hand), then add 1–2 drops of diluted $KMnO_4$ solution

(1 cc. of the laboratory reagent plus 9–10 cc. of H_2O). If $C_2O_4^{--}$ is present, the color will fade to a tan and then disappear completely. If a few drops more of the $KMnO_4$ solution are added, the color will now disappear more promptly, due to the catalytic effect of the Mn^{++}.

$$5\ H_2C_2O_4 + 6\ HNO_3 + 2\ KMnO_4 = 10\ CO_2 + 2\ Mn(NO_3)_2 + 2\ KNO_3 + 8\ H_2O$$

4. Another test for oxalate radical, called the *carbon dioxide test*, makes use of the fact that oxalic acid is readily oxidized to CO_2 by $KMnO_4$. Any CO_3^{--} is first removed by acidifying slightly and then boiling out all CO_2; the solution is then made more strongly acid with HNO_3, treated with 2–3 cc. of $KMnO_4$ solution (full strength reagent), and heated, applying the test for CO_2 again. If a further test for CO_2 is obtained, this is evidence of the presence in the solution of carbon, other than carbonate, in a form fairly readily oxidized to CO_2. Since CO_3^{--} and $C_2O_4^{--}$ are the only forms of carbon being studied, this procedure becomes a test for $C_2O_4^{--}$.

Test for Arsenate Radical

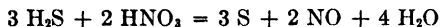
§271. **Manipulation.** — To 2–3 cc. of the original solution add 3–5 cc. of 5 *N* HCl, heat nearly to boiling, and treat with H_2S. A bright yellow precipitate will form if H_3AsO_4 is present.

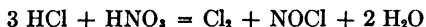
$$2\ H_3AsO_4 + 5\ H_2S = As_2S_5 + 8\ H_2O$$

Filter, test the filtrate for completeness of precipitation, and set it aside for the phosphate test (§273). Wash the precipitate thoroughly and test it for As according to the procedures employed in Group II of the metals (p. 272, §87, §88, 4, 5).

§272. **Notes.** — 1. In treating As as one of the Group II metals, the problem of precipitation of As_2S_5 was considered in some detail. The chief purpose of including AsO_4^{-3} among the acid radicals is to emphasize its interference with the test for PO_4^{-3} and the necessity of its removal before applying a test for the latter.

2. Occasionally the solution will contain reagents that react with the H_2S used for precipitation of As_2S_5, causing the precipitation of S°, and even interfering with the precipitation of the As. Thus, a solution containing any considerable quantity of NO_3^-, on making strongly acid with HCl and heating, becomes a fairly strong oxidant. Under such conditions a heavy precipitate of S° may form and the precipitation of As_2S_5 will be incomplete until much of the nitric acid has been reduced by the H_2S.

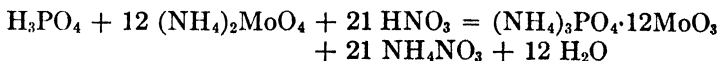
$$3\ H_2S + 2\ HNO_3 = 3\ S + 2\ NO + 4\ H_2O$$

If such a case is encountered, it may be simplest to add 10–15 cc. of HCl and evaporate to approximate dryness to remove most of the HNO_3.

$$3\ HCl + HNO_3 = Cl_2 + NOCl + 2\ H_2O$$

Other oxidants besides NO_3^-, will interfere in a similar way. One of these, H_2SO_3, ordinarily classed as a reductant, is of some particular interest because it will oxidize H_2S to S°, but it would also reduce H_3AsO_4 to H_3AsO_3, so AsO_4^{-3} would not be present in a solution containing this substance.

3. Because of the possibility of obtaining a precipitate of S° on treating the solution with H_2S, it is necessary to examine the precipitate further for As. If there is a moderate amount of As_2S_5, its bright yellow color and flocculent character do not require further identification. But a small amount of As_2S_5 may be masked to such an extent that the confirmatory test becomes necessary.

Test for the Phosphate Radical

§273. Manipulation. — If arsenic is absent, as shown by the previous test (§271), a portion of the original solution may be used directly in the test for PO_4^{-3}. To 2–3 cc. of the original solution add 3–5 cc. of HNO_3 and 8–10 cc. of $(NH_4)_2MoO_4$, warm slightly, and look for the formation of a bright yellow precipitate of ammonium phosphomolybdate.

$$H_3PO_4 + 12\ (NH_4)_2MoO_4 + 21\ HNO_3 = (NH_4)_3PO_4{\cdot}12MoO_3 + 21\ NH_4NO_3 + 12\ H_2O$$

If arsenic is present in the original solution, use the filtrate from the As_2S_5 (§271). After making certain that the As is completely precipitated, evaporate the solution barely to dryness, then add 10 cc. of 5 *N* HNO_3 and evaporate again barely to dryness. Add 5 cc. of HNO_3, and then test for PO_4^{-3} as above.

§274. Notes. — 1. The precipitation of $(NH_4)_3PO_4{\cdot}12MoO_3$ depends upon the combining of molybdic anhydride with phosphoric acid, forming a complex acid, $H_3PO_4{\cdot}12MoO_3$, phosphomolybdic acid, whose ammonium salt is insoluble in nitric acid. Since there are other phosphomolybdic acids — containing less MoO_3 than this one — whose ammonium salts are appreciably more soluble, it is important to add a sufficient amount of the reagent to exceed the ratio of 12 atoms of Mo to 1 of P. For this reason the reagent is added in relatively large amounts.

2. The precipitate forms slowly from a cold solution, especially when only a small amount of phosphate is present. When heated to approximately 60°, precipitation takes place much more readily. It is desirable to keep the temperature distinctly below the boiling point, however, otherwise the reagent may undergo decomposition with separation from solution of a light yellow, hydrated molybdic anhydride, $MoO_3{\cdot}H_2O$, which might be mistaken for a test for phosphate. (The readiness with which this reaction occurs at temperatures near the boiling point, means that precipitates of ammonium phosphomolybdate formed under such conditions will be contaminated with appreciable amounts of MoO_3. In quantitative analysis, therefore, it is necessary to set up a proper relation between temperature and time allowed for completeness of precipitation, in order to obtain a precipitate of definite composition.)

3. The chemical similarity of As and P, which would be expected from their adjacent positions in the fifth column of the Periodic Table, is exemplified in the existence of arsenomolybdic acid, $H_3AsO_4{\cdot}12MoO_3$, whose ammonium salt is bright yellow in color and precipitates readily in hot HNO_3 solution. The precipitate does not form so readily at lower temperatures as does the phosphomolybdate, so moderate amounts of H_3PO_4 can be identified without removal of As, by trying the test with $(NH_4)_2MoO_4$ in the cold. This procedure is uncertain, however, for low concentrations of H_3PO_4.

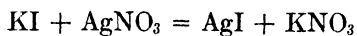
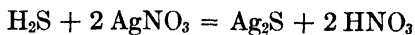
4. The precipitate is appreciably more soluble in HCl than in HNO_3, therefore after the precipitation of As_2S_5 in strong HCl solution, it is desirable to remove the free HCl by evaporation, and even to oxidize chloride ion to chlorine by adding HNO_3 and evaporating again.

5. Occasionally, on adding $(NH_4)_2MoO_4$ to an unknown solution, the color turns blue, blue green, or brown. This is due to the presence of reductants such as H_2SO_3, I^-, and H_2S, which reduce some of the molybdenum to the quadrivalent form (possibly $MoO(NO_3)_2$), whose compounds are blue or blue green. With H_2S a sulfur derivative may be obtained, brown in color, from which a sulfide of molybdenum slowly precipitates. These sources of confusion may be avoided by adding moderate excess of HNO_3 and evaporating to approximate dryness, which will effectively remove the stronger reductants. Or the PO_4^{-3} may be precipitated with excess of $CaCl_2$ or $MgCl_2$ in ammoniacal solution, the precipitate being filtered out, washed thoroughly, and dissolved in HNO_3. The resulting solution is then treated with $(NH_4)_2MoO_4$ as usual.

PROCEDURE FOR THE ANALYSIS FOR GROUP II ANIONS

§275. **Manipulation.** — Place 2–3 cc. of the original solution in a test tube. Test with litmus paper. If alkaline, acidify with HNO_3. Add sufficient excess of HNO_3 to make the solution 1.5–2 *N* with HNO_3, then add 0.5 cc. of $AgNO_3$ solution. If H_2S is present, a black precipitate of Ag_2S will form. With I^-, Br^-, or Cl^-, a pale yellow to white precipitate will form.

$$H_2S + 2\,AgNO_3 = \underline{Ag_2S} + 2\,HNO_3$$

$$KI + AgNO_3 = \underline{AgI} + KNO_3$$

If Group II anions are present, proceed with the tests for the individual anions. (§§277–84.)

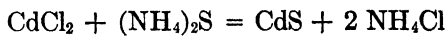
§276. **Notes.** — 1. Silver sulfide precipitates in the presence of cold 2 *N* HNO_3, but it dissolves fairly readily (through oxidation to S) on heating with this reagent. Therefore it is necessary to have the solution cold in order to recognize the smaller concentrations of sulfide radical.

2. Silver sulfide is less soluble than the silver halides (even AgI), and is black in color, so one cannot judge concerning the presence or absence of halides on the basis of this preliminary test when sulfide is present.

3. The silver salts of the Group 1 acid radicals are insoluble in water (Ag_2SO_4 is slightly soluble), but they may be prevented from precipitating by having a moderate amount of free HNO_3 present in the solution and adding only a small amount of $AgNO_3$. $Ag_2C_2O_4$ and Ag_2SO_3 are sufficiently insoluble even in dilute HNO_3 so that failure to add sufficient HNO_3 or the use of too much $AgNO_3$ may result in the formation of a white flocculent or granular precipitate, even though Group II anions are absent. In case of doubt, add several cc. more of HNO_3 and heat. Silver oxalate or sulfite will dissolve, but the silver halides are relatively insoluble even in hot HNO_3, so they will remain as precipitates after this treatment.

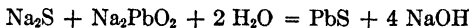
Test for Sulfide Radical

§277. **Manipulation.** — Place 2–3 cc. of the original solution in a test tube. Test with litmus paper. Add 3–5 cc. of NH_4Cl and 3–4 cc. excess of NH_4OH, then add 0.5 cc. of $CdCl_2$ solution. A bright yellow or greenish-yellow precipitate indicates a sulfide.

$$CdCl_2 + (NH_4)_2S = \underline{CdS} + 2\,NH_4Cl$$

§278. **Notes.** — 1. This test depends upon the fact that CdS has a characteristic color, and is so insoluble that it will precipitate even in a strongly ammoniacal solution. In the absence of S^{--}, the Cd^{++} would change directly to the colorless $Cd(NH_3)_4^{++}$, which furnishes so low a concentration of Cd^{++} that none of the other Cd salts will precipitate. Sometimes the $CdCl_2$ is converted to $Cd(NH_3)_4Cl_2$ before it is added to the solution, thus leaving the excess NH_4OH undisturbed. If only a small amount of $CdCl_2$ is used, however, this is an unnecessary precaution.

2. Another reagent frequently used is sodium plumbite, Na_2PbO_2. This reagent is prepared by treating 1 cc. of $Pb(NO_3)_2$, or $Pb(C_2H_3O_2)_2$, solution with just sufficient excess of NaOH to dissolve the precipitate of $Pb(OH)_2$ which first forms. A portion of

the original solution is treated with several cc. excess of NaOH, and then the Na_2PbO_2 added. A black precipitate of PbS indicates a sulfide.

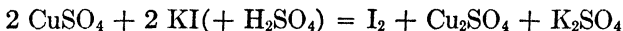
$$Na_2S + Na_2PbO_2 + 2\ H_2O = \underline{PbS} + 4\ NaOH$$

If sufficient excess of NaOH is present, only PbS will precipitate.

3. These tests are rather more delicate than the original Group II test, because of the high concentration of HNO_3 present in the latter case, and the possible dilution of the black color by the silver halides. Further, with SO_3^{--} present, or strong oxidants, when the solution is made strongly acid with HNO_3 the H_2S may be oxidized to $S°$ and the test lost.

4. An alternative test frequently used, consists in acidifying the solution slightly with $HC_2H_3O_2$ (HCl or H_2SO_4), then heating and testing the vapors above the solution with lead acetate paper. (The latter is prepared by putting a few drops of $Pb(C_2H_3O_2)_2$ solution on a strip of filter paper.) A brown or black stain of PbS will form on the test paper if H_2S is give off. This test depends upon the fact that H_2S is a weak acid and only slightly soluble in water, so if the solution is acidified and heated, the H_2S will be given off readily. As a matter of fact, H_2S is so weak an acid that $(NH_4)_2S$ and even Na_2S are largely hydrolyzed in aqueous solution. Therefore it is not necessary to add a strong acid or to add a large excess in order to convert S^{--} effectively into H_2S. It is feasible to use excess of NH_4Cl to lower the concentration of OH^- (and raise the concentration of H^+) to such an extent that H_2S may be boiled out of the solution.

Test for Iodide Ion

§279. **Manipulation.** — If sulfide radical is present, this should be removed before the test for I^- is applied. Place 2–3 cc. of the original solution in a test tube and acidify with H_2SO_4 adding 1–2 cc. excess of the 5 *N* acid. If sulfide is present, heat until the vapors no longer give a test with $Pb(C_2H_3O_2)_2$ paper. Cool, filter if necessary, add about 0.5 cc. of CCl_4, and 2–3 cc. of $CuSO_4$ solution, shake vigorously, and let stand a moment until the CCl_4 globule collects again. A pink color in the CCl_4 is an indication that I^- is present.

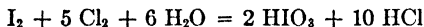
$$2\ CuSO_4 + 2\ KI(+\ H_2SO_4) = I_2 + Cu_2SO_4 + K_2SO_4$$

§280. **Notes.** — 1. The purpose of removing sulfide radical is to increase the sharpness of the reaction of the oxidant with iodide ion. Hydrogen sulfide is a stronger reductant than iodide ion, therefore it would use up the first portion of any oxidant added, making it necessary to use sufficient reagent to be more than equivalent to the H_2S before any free iodine would be obtained. Further, the precipitate of sulfur (and CuS in case $CuSO_4$ is used as oxidant) would collect with the CCl_4 at the bottom of the test tube, making it difficult to judge the color of the latter. With H_2S removed, the oxidant reacts directly and promptly with any iodide present.

2. Copper sulfate is used to oxidize the I^- to I_2, because it is a mild oxidant which will not set bromine free or convert I_2 to IO_3^-. For this reason, it may be used in moderate amount without danger of interference in the identification of I^- in the lower concentrations.

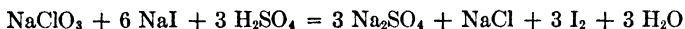
3. If one wishes to test for rather small amounts of I^- it may be necessary to increase the concentration of H_2SO_4 to 5 *N* or higher. If the test above is negative, cool the solution thoroughly and add carefully 1 cc. of concentrated H_2SO_4 (or, better, add 1 cc. of concentrated H_2SO_4 to 1 cc. of H_2O, cool, and add this to the solution). Shake, let stand a moment, and again note the color of the CCl_4 layer.

4. Many other oxidants may be used instead of $CuSO_4$ to oxidize I^- to I_2. Thus, Fe^{+3}, HNO_2, Cl_2-water, and $K_2S_2O_8$ are frequently used for this purpose. All of these are stronger oxidants than Cu^{++}, ranging from Fe^{+3}, which is still fairly mild, to $K_2S_2O_8$,

which, under proper conditions, will even oxidize Mn^{++} to MnO_4^- in acid solution. Under properly controlled conditions, satisfactory results can be obtained with any of these reagents. Ferric ion ($FeCl_3$ or $Fe_2(SO_4)_3$) may be added in moderate quantities in the presence of *N* to 5 *N* HCl or H_2SO_4. Nitrous acid is added in the form of $NaNO_2$ in an acetic acid solution containing a small amount of $NaC_2H_3O_2$. Chlorine water, in dilute HCl solution, must be added cautiously in small amounts at a time, to identify lower concentrations of I^-. If too much is used, the I^- is oxidized beyond I_2 to IO_3^-, which will not impart color to the CCl_4 layer.

$$I_2 + 5\ Cl_2 + 6\ H_2O = 2\ HIO_3 + 10\ HCl$$

Potassium persulfate (or $(NH_4)_2S_2O_8$) may be used in moderate amounts, but the solution should be only slightly acid with $HC_2H_3O_2$ and should contain a moderate amount of $NaC_2H_3O_2$ or $NH_4C_2H_3O_2$.

5. If ClO_3^- is present along with I^- (in a neutral or alkaline solution), iodine will be set free when the solution is acidified.

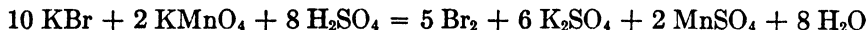
$$NaClO_3 + 6\ NaI + 3\ H_2SO_4 = 3\ Na_2SO_4 + NaCl + 3\ I_2 + 3\ H_2O$$

This does no particular harm if the solution is kept cold and treated immediately with CCl_4 to identify the I_2; but if the solution becomes warm, the I_2 is oxidized fairly readily to IO_3^-, so the test for I^- may be lost, and Cl^- may be present that was not there originally.

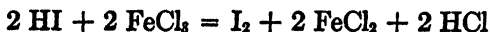
$$3\ I_2 + 5\ NaClO_3 + 3\ H_2O = 5\ NaCl + 6\ HIO_3$$

6. CCl_4 is used as a colorless solvent, insoluble in water, to separate the free iodine from a colored solution, and to concentrate the iodine so that its color may be the more readily visible. Since iodine is about 80 times as soluble in CCl_4 as in water, the iodine will continue to dissolve in the CCl_4 until the concentration in the latter is essentially 80 times that in the water. But if equal volumes of CCl_4 and solution are used, the concentration of iodine in the CCl_4, at equilibrium, will be slightly less than in the aqueous solution originally. On this basis, there will be no increased delicacy of the test (in the absence of other colored substances), unless a new color is obtained which is more visible than the tan of the aqueous iodine solution. However, if the volume of CCl_4 added is considerably less than that of the aqueous solution, the concentration of I_2 in the CCl_4, at equilibrium, will be correspondingly greater than in the original aqueous solution. Therefore, the delicacy of the test increases almost directly with the smallness of the volume of CCl_4 added.

Test for Bromide Ion

§281. Manipulation. — If sulfide and iodide are absent, place 2–3 cc. of the original solution in a test tube, neutralize if alkaline, and add 1–2 cc. of 5 *N* H_2SO_4. Add 0.5 cc. of CCl_4 and a few drops of $KMnO_4$ solution, shake thoroughly, and let the solution stand a moment until the CCl_4 settles. If bromide is present the CCl_4 layer will be colored light brown.

$$10\ KBr + 2\ KMnO_4 + 8\ H_2SO_4 = 5\ Br_2 + 6\ K_2SO_4 + 2\ MnSO_4 + 8\ H_2O$$

If sulfide is present, it may be removed as indicated under Test for Iodide Ion (§279). If iodide ion is present, the solution (after removal of sulfide) is treated with 1–2 cc. of 5 *N* H_2SO_4, then 5 cc. of $FeCl_3$ solution is added, and the solution is heated in the casserole until the iodine is all vaporized (the purple iodine vapors no longer appear and the solution is light yellow in color, like $FeCl_3$).

$$2\ HI + 2\ FeCl_3 = I_2 + 2\ FeCl_2 + 2\ HCl$$

Cool, add slight excess of $KMnO_4$, shake thoroughly, add 0.5 cc. of CCl_4 and shake again, then add a few drops of H_2O_2 to convert any $KMnO_4$ or MnO_2 to colorless $MnSO_4$, and note the color of the CCl_4 layer.

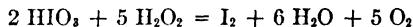
Notes. — 1. Many other oxidants may be used instead of $KMnO_4$ to oxidize Br^- to Br_2. Among the more common ones are Cl_2-water, used in dilute HCl or H_2SO_4 solution; $K_2S_2O_8$, used in dilute H_2SO_4 solution and requiring heat for ready action; $K_2Cr_2O_7$, used in dilute HCl or H_2SO_4 solution and requiring heat; and concentrated HNO_3, also requiring some warming for ready action. $KMnO_4$ has one advantage, that its color shows when excess has been added, so one need never worry about not having used sufficient to oxidize the Br^-. Further, the color is easily removed by a few drops of H_2O_2, without danger of losing the test for Br_2.

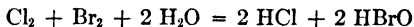
2. It is important to add slight excess of $KMnO_4$ in looking for traces of Br^-, because failure to vaporize the I_2 completely might result in obtaining an iodine-colored layer of CCl_4. With excess of $KMnO_4$, any free iodine is readily oxidized to IO_3^-.

$$2\ KMnO_4 + I_2 + 3\ H_2SO_4 = 2\ HIO_3 + K_2SO_4 + 2\ MnSO_4 + 2\ H_2O$$

Since IO_3^- does not impart color to the CCl_4, and is only slowly reduced again to I_2 in cold, dilute solution by the H_2O_2, there is no further danger of interference from the I_2 under ordinary conditions of manipulation.

3. It is not feasible to use excess of $KMnO_4$ to convert any considerable quantity of I^- to IO_3^- and then reduce the excess of MnO_4^- with H_2O_2, because of the readiness with which H_2O_2 will react with IO_3^- when the latter is present in moderate amounts, liberating I_2 again.

$$2\ HIO_3 + 5\ H_2O_2 = I_2 + 6\ H_2O + 5\ O_2$$

4. It is possible to convert I^- to IO_3^- by adding Cl_2-water in small amounts at a time to the slightly acid solution, shaking thoroughly after each addition, and continuing this until the color due to free iodine has nearly disappeared. Then add a little CCl_4 and a little more Cl_2-water and shake again. If the I_2 is left in small enough amounts, the Cl_2-water will be sufficient to complete the oxidation of this to IO_3^- and to set free some Br_2, which will dissolve in the CCl_4. If the CCl_4 has an iodine color, the solution may be poured through a wet filter paper (the CCl_4 will not run through) and the filtrate treated again with CCl_4 and Cl_2-water. Any large excess of Cl_2-water must be avoided, since this decreases to some extent the delicacy of the test for Br_2.

$$Cl_2 + Br_2 + 2\ H_2O = 2\ HCl + 2\ HBrO$$

5. Another reagent, commercially available though not in general use as yet, is neutral hypochlorite solution. Calcium hypochlorite (not bleaching powder) is now available as an inexpensive solid, containing 65% hypochlorite radical. A 5% solution of this in water serves all the purposes of chlorine water, but is much more stable and supplies a much higher concentration of oxidant. Experiments at the University of Michigan by Doctor Carney and Doctor Soule indicate the value of this reagent in both qualitative and quantitative analysis. The neutral sodium hypochlorite solutions, sold at the grocery stores under the names "Chlorox" and "Oxol," may serve equally well.

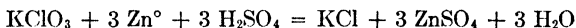
If a solution containing a moderate amount of I^-, is treated with dilute sulfuric acid and then this reagent is added about 1 cc. at a time, the solution turns brown with formation of I_3^-; then a black precipitate of I_2 forms, which, on continued shaking and addition of slight excess of the reagent, dissolves fairly promptly to give the colorless IO_3^-. If Br^- is present at the same time, this will be oxidized to Br_2 by the excess of ClO^-, the Br_2 being oxidized somewhat further by large excess of the reagent. Thus it is possible to carry out the test for both I^- and Br^- on a single portion of the solution as follows: Place 2–3 cc. of the solution in a test tube, add an equal volume of 5 *N* H_2SO_4, add 0.5 cc. of CCl_4, then add carefully a small drop of the reagent and shake thoroughly. (It is important to use a very small amount of the reagent in this first step so as to be able to identify a reasonably small quantity of I^-. If too much reagent is added, the test will be missed because of the rapidity with which the oxidation to IO_3^- takes place.) After the test for I^- has been obtained, add about 1 cc. of the reagent and shake. If the

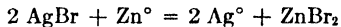
amount of I^- is small and Br^- is present, the I_2 color in the CCl_4 will be replaced by Br_2. If the amount of I^- is moderate or large, the solution will become deep brown. Add more reagent, about 1 cc. at a time, until the iodine has all precipitated and started to redissolve. If the amount of I_2 precipitated is large, it may save time to filter, removing I_2 and the CCl_4 globule in this way. Then add more CCl_4 and another cc. of the reagent, and shake again. If Br^- is present, the characteristic color will be obtained. It is possible to oxidize all the I_2 to IO_3^- instead of filtering as just suggested, but the reaction with the solid I_2 is a little slow, so the solution must be shaken vigorously for 10–15 seconds between additions of the hypochlorite.

6. Another interesting procedure for separating the iodine from the solution consists in adding 5 cc. of CCl_4 to the cold solution (after treatment with $FeCl_3$), then shaking vigorously for a moment or two and filtering through a wet filter paper. Much of the I_2 will dissolve in the CCl_4, which will be retained on the filter paper. The filtrate may be treated again with CCl_4 (sometimes a third treatment is necessary), which will usually reduce the concentration of I_2 in the solution to such an extent that the rest can be oxidized to IO_3^- by excess of $KMnO_4$ as indicated in note 2. To obtain an appreciation of the importance of the time allowed for the dissolving of the I_2 in the CCl_4 in this experiment, it is worth while to try this procedure with known solutions, extracting with fresh portions of CCl_4 until the I_2 color becomes very faint, and then calculating the completeness of removal that should result from two extractions if equilibrium were reached in each case.

7. An alternative procedure to oxidize the I^- to I_2 and remove it by boiling, uses $K_2S_2O_8$ in a dilute acetic acid solution containing $NH_4C_2H_3O_2$. This will be described in detail under Cl^-, as part of a general procedure for identifying I^-, Br^- and Cl^- on a single portion of the original solution (§284, 5).

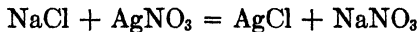
8. If ClO_3^- is present, the I_2 cannot be removed by volatilization with heat from a moderately acid solution, because ClO_3^- is a strong enough oxidant under these conditions to oxidize Br^- to Br_2, so the bromine might be lost in the procedure aimed at preparing the solution for the test. So far as the test for Br^- is concerned, it is possible to overcome this interference of ClO_3^- by reducing the ClO_3^- to Cl^- by treating the acid solution for a short time with metallic zinc.

$$KClO_3 + 3\ Zn^\circ + 3\ H_2SO_4 = KCl + 3\ ZnSO_4 + 3\ H_2O$$

Or it is possible to separate the Br^- by precipitating with excess of $AgNO_3$ in the original solution (neutralized if alkaline). The ClO_3^- remains in solution. After filtering and washing, the precipitate is placed in a beaker, treated with 2–3 cc. of H_2O, a few drops of concentrated H_2SO_4, and with 0.5–1.0 g. Zn° (about 20 mesh). Warm slightly and let stand 2–3 minutes, with occasional shaking.

$$2\ AgBr + Zn^\circ = 2\ \underline{Ag^\circ} + ZnBr_2$$

Filter, discard the precipitate ($Ag^\circ + Zn^\circ$), and test the filtrate in the usual way for Br^-

Test for Chloride Ion

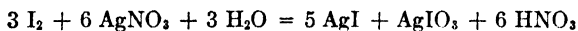
§283. Manipulation. — In the absence of sulfide, iodide and bromide, place 2–3 cc. of the original solution in a test tube, neutralize if alkaline, add 3–4 cc. of 5 *N* HNO_3 and 0.5 cc. of $AgNO_3$ solution. A curdy, white precipitate indicates a chloride.

$$NaCl + AgNO_3 = \underline{AgCl} + NaNO_3$$

If sulfide radical is present, it may be removed by the procedure described under Test for Iodide (§279). If iodide and bromide are present, measure out 5 cc. of the solution (after removal of H_2S if necessary) into an Erlen-

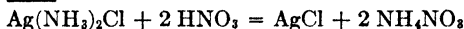
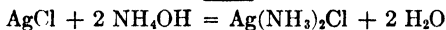
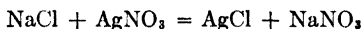
meyer flask, cool thoroughly and add cautiously, with cooling, 4–5 cc. of concentrated H_2SO_4. Then add 5 cc. of acetone (free from reducing agents), and cool thoroughly again. To the cold solution add $KMnO_4$ carefully, 2–3 drops at a time, with swirling, until a faint color of MnO_4^- appears. Add a few drops of H_2O_2 to reduce the MnO_4^-, and then add 0.5 cc. of $AgNO_3$ to test for Cl^-.

§284. **Notes.** — 1. In testing for Cl^-, it is necessary to add sufficient HNO_3 to prevent the precipitation of $Ag_2C_2O_4$ or Ag_2SO_3, both of which are white (although flocculent rather than curdy).

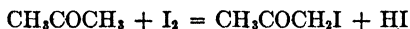
2. If iodide is present, but no bromide, the I^- may be removed as described in §281, by treatment with excess of $Fe_2(SO_4)_3$ (free from Cl^-) in dilute H_2SO_4 solution, and then boiling to vaporize all the iodine. In this case it is necessary to be more careful to boil out the I_2 completely, since oxidation to IO_3^- will not prevent its interference with the test for Cl^-.

$$3\ I_2 + 6\ AgNO_3 + 3\ H_2O = 5\ \underline{AgI} + \underline{AgIO_3} + 6\ HNO_3$$
$$HIO_3 + AgNO_3 = \underline{AgIO_3}\ (\text{white}) + HNO_3$$

After complete removal of I_2, the solution is treated with 0.5 cc. $AgNO_3$ to precipitate any Cl^- as AgCl. This is a simpler procedure than the one described above and should be used when Br^- is absent.

3. Another procedure in testing for Cl^- in the solution containing I^-, depends on the marked difference in solubility of AgI and AgCl in dilute NH_4OH. Treat the solution with excess of $AgNO_3$, filter, and wash. Transfer the precipitate to a test tube, pour off any excess H_2O, then add 5 cc. of 2 *N* NH_4OH, shake for a moment and filter. To the filtrate, add excess HNO_3 (sufficient to redissolve any $Ag_2C_2O_4$ if oxalate was present in the original solution), and look for a curdy, white precipitate of AgCl.

$$NaCl + AgNO_3 = \underline{AgCl} + NaNO_3$$
$$\underline{AgCl} + 2\ NH_4OH = Ag(NH_3)_2Cl + 2\ H_2O$$
$$Ag(NH_3)_2Cl + 2\ HNO_3 = \underline{AgCl} + 2\ NH_4NO_3$$

This procedure cannot be used, however, to determine small amounts of Cl^- in the presence of Br^-, because of the slight solubility of AgBr in 2 *N* NH_4OH, so that a visible precipitate will be obtained even in the absence of chloride. With moderate amounts of Cl^-, a sufficiently heavy precipitate will be obtained to be easily distinguished from the small precipitate due to AgBr.

4. In the acetone-permanganate method described above, the acetone absorbs the I_2 and Br_2 with formation of iodo-acetone and bromo-acetone, which will not give precipitates with $AgNO_3$. In the absence of accessory oxidant, only half the halogen would be absorbed.

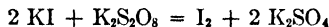
$$CH_3COCH_3 + I_2 = CH_3COCH_2I + HI$$

But if MnO_4^- is added at the same time, the I_2 is completely converted to iodo-acetone.

$$10\ CH_3COCH_3 + 5\ I_2 + 2\ KMnO_4 = 10\ CH_3COCH_2I + K_2SO_4 + 2\ MnSO_4 + 8\ H_2O$$

As soon as the halogen is all converted to the acetone halide, the excess of permanganate will be easily recognized. In order to get a sharp reaction with the last trace of bromine, it is necessary to have the solution 10–12 *N* with sulfuric acid. Further, the solution should be kept well cooled in running water. If the solution is much more acid than that, or if it becomes warm, there may be appreciable loss of Cl^- as excess of MnO_4^- is added. The permanganate color fades rather promptly to a light pink, which is fairly stable. As soon as the endpoint is obtained, the solution should be swirled to rinse down any drops which have spattered onto the walls of the flask, and the excess MnO_4^- immediately reduced with a few drops of H_2O_2, to prevent further action on any Cl^-. Under

proper conditions, however, the method is adequate for the quantitative determination of traces of Cl^- in bromides.[1]

5. Another method frequently used for oxidation of Br^- to bromine, followed by boiling the solution to remove the Br_2, employs $K_2S_2O_8$ in dilute solution, in the presence of approximately 0.5 N HNO_3 or H_2SO_4. Since this same reagent may be used under proper conditions to oxidize I^- to I_2 and remove the iodine without loss of Br^-, it is possible to carry out the successive identification of I^-, Br^- and Cl^- on a single portion of the original solution through the application of this reagent. The procedure employed, called the *persulfate method* for separating and identifying the halides, is as follows: To 10 cc. of the original solution (after removal of sulfide and separation from ClO_3^-), add 5 cc. of 5 N NH_4OH, then acidify with acetic acid, adding 2–3 cc. excess. Dilute with water to 60–70 cc., add 0.5 g. $K_2S_2O_8$ (or $(NH_4)_2S_2O_8$), and warm slightly. If a tan to brown color develops, pour off a 5–10 cc. test portion of the solution into a test tube, cool, add 0.5 cc. CCl_4, shake, and look for the characteristic iodine color in the CCl_4.

$$2\ KI + K_2S_2O_8 = I_2 + 2\ K_2SO_4$$

After the test for I_2 has been made, heat the solution to boiling and let it boil gently until it becomes colorless, adding small quantities of water from time to time to prevent decrease in volume of the solution. When colorless, let the solution cool slightly, add 0.5 g. more of $K_2S_2O_8$, and note whether further color develops. If it does, boil till colorless and repeat the test. When no further color develops, the I^- may be considered to be completely oxidized to I_2 and volatilized from the solution. Next, to test for Br^-, pour 2 cc. of concentrated H_2SO_4 into 10 cc. of H_2O, and add this to the main solution. Add 0.5 g. of $K_2S_2O_8$, heat just to the boiling point, then remove from the flame and let stand a moment or two for the oxidation of Br^- to Br_2. If a yellow color develops, take a 10 cc. test portion of the solution, cool thoroughly, and add CCl_4 as usual, to identify the Br_2.

$$2\ KBr + K_2S_2O_8 + 2\ H_2SO_4 = Br_2 + 4\ KHSO_4$$

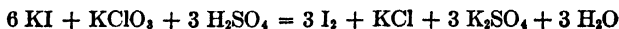
Following the test for Br^-, boil the solution till colorless, keeping the volume of the solution up by adding water as necessary. When the solution is colorless, let cool slightly, add 0.5 g. of $K_2S_2O_8$, heat to boiling, and note whether any further color develops. If not, boil the solution 2–3 minutes longer to oxidize and remove the last bit of Br^-, then cool and treat with 0.5 cc. of $AgNO_3$ solution. If Cl^- is present, a marked opalescence or curdy, white precipitate will form.

The persulfate method illustrates in an interesting way the effect which a change in concentration of H^+ may have on the oxidizing power of a reagent. In a dilute acetic acid solution, containing excess of acetate ion, $S_2O_8^{--}$ is a mild enough oxidant, so that it will oxidize I^- to I_2, but will not attack dilute Br^- even at the boiling point. By raising the concentration of H^+ to that of 0.5–0.8 N H_2SO_4, the oxidizing power of the $S_2O_8^{--}$ is increased sufficiently so that it will oxidize Br^- fairly readily when heated, but will not oxidize dilute Cl^-. At still higher concentrations of H^+, Cl^- may be oxidized to Cl_2 by this same reagent. In the procedure as described, the volume of the solution is important as well as the quantities of reagents added, in order to control the acidity of the solution and the concentrations of halide ions presented for oxidation.

The persulfate method, carefully used, gives entirely satisfactory results for moderate quantities of the halides. It works well for small amounts of I^- and Cl^-, but not so well for small amounts of Br^-, due to the slowness of the oxidation, permitting the Br_2 to volatilize as it is formed, without developing visible color. For this reason, it would be best to test for Br^- after removal of I_2, by taking a 10 cc. test portion of the solution, cooling, and adding a few drops of $KMnO_4$ solution. Add CCl_4 and shake, then decolorize the aqueous solution if necessary, with a few drops of H_2O_2.

6. If ClO_3^- is present, it is impossible to carry out the usual procedures of removal of I^- and Br^- in acid solution before testing for Cl^-, because the ClO_3^- will be reduced more or less to Cl^- under these conditions, so a test for Cl^- would be obtained, even though it was not present at the start.

$$6\ KI + KClO_3 + 3\ H_2SO_4 = 3\ I_2 + KCl + 3\ K_2SO_4 + 3\ H_2O$$

$$6\ I_2 + 10\ KClO_3 + 6\ H_2O = 12\ HIO_3 + 2\ KCl$$

[1] McAlpine, *J. Am. Ch. Soc.*, **51**, 1065 (1929).

In this case, the simplest procedure is that recommended in §282, 8, precipitating the halides in neutral solution with excess of $AgNO_3$, filtering, washing thoroughly, and then getting the halides into solution again by treating the precipitate with metallic Zn in the presence of dilute H_2SO_4. Filter, discard the precipitate (Zn° and Ag°), and test the filtrate in the usual way for I^-, Br^- and Cl^-.

PROCEDURE FOR THE ANALYSIS FOR GROUP III ANIONS

§285. **Manipulation.** — Place 2–3 cc. of the original solution in a test tube, neutralize if alkaline, and add 5 cc. excess of 5 *N* H_2SO_4. Add 2 cc. of 0.1 *N* KI solution. If ClO_3^- is present in moderate amount, or NO_3^- in large amount, a brown color of KI_3 will develop. Extract with CCl_4 to obtain the characteristic iodine color.

$$KClO_3 + 3\ H_2SO_4 + 9\ KI = 3\ KI_3 + KCl + 3\ K_2SO_4 + 3\ H_2O$$

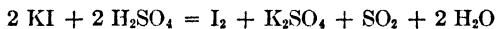
$$2\ KNO_3 + 4\ H_2SO_4 + 9\ KI = 3\ KI_3 + 2\ NO + 4\ K_2SO_4 + 4\ H_2O$$

If no color develops, repeat the test as follows: To 4 cc. of the solution (after neutralization) add 2 cc. of concentrated H_2SO_4, cautiously, and with thorough cooling. Then add 2 cc. of 0.1 *N* KI solution. If no color develops immediately, warm the solution slightly (to 40°–45°), and extract with 0.5 cc. of CCl_4 to concentrate any iodine into a small volume. If iodine color develops, proceed with the individual tests for ClO_3^- and NO_3^-.

§286. **Notes.** — 1. This test depends upon the fact that the two anions considered in Group III, ClO_3^- and NO_3^-, are fairly strong oxidants in acid solution, while I^- is fairly readily oxidized to free iodine, which is easily identified even in quantities of 1 mg. or less.

2. Chlorate ion is a stronger oxidant than NO_3^- and thus will give a positive test in the above procedure more readily than the latter. The oxidizing potentials of both are decreased as the solution becomes more dilute, but are increased by increasing the acidity of the solution. Thus, if the concentrations of ClO_3^- and NO_3^- are sufficiently low, the test will fail in dilute acid solution, but will become positive as the acidity of the solution is increased. By carrying out the test in two stages (1st, in 2–3 *N* H_2SO_4 solution, 2nd, in 9–10 *N* H_2SO_4 solution if the first results are negative), valuable indications can be obtained as to the relative quantities of Group III anions present.

3. In using concentrated H_2SO_4 to make the solution strongly acid, and in warming the solution slightly to look for very small amounts of Group III anions, due account must be taken of the oxidizing action of H_2SO_4 itself. With too high a concentration of H_2SO_4, or on heating too strongly, iodine may be liberated through reaction with the H_2SO_4.

$$2\ KI + 2\ H_2SO_4 = I_2 + K_2SO_4 + SO_2 + 2\ H_2O$$

The directions given are adequate to avoid this difficulty, except in the case covered in the following note.

4. If the original solution contains I^- as well as Group III anions, color may develop directly on acidifying the solution. In this case, it is only necessary to extract with CCl_4 to identify the iodine (or possibly Br_2). If iodide is present and no color develops in the dilute acid solution, unusual care must be taken in preparing the solution for the identification of smaller quantities of Group III anions, otherwise the difficulty mentioned in note 3 may occur. On pouring concentrated H_2SO_4 into a dilute I^- solution, the heat of dilution as well as local areas of high acidity in the solution may easily lead to libera-

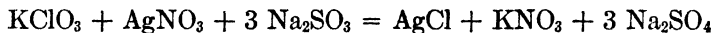
tion of iodine without Group III anions being present. By very careful manipulation this difficulty may be avoided, even using concentrated H_2SO_4; but it is much simpler to prepare some 1–1 H_2SO_4 (one volume of concentrated H_2SO_4, carefully poured into an equal volume of water), using 4–5 cc. of this in place of the 2 cc. of concentrated H_2SO_4. Even in this case, the solution should be kept cold with running water while the H_2SO_4 is being added.

5. Other oxidants besides ClO_3^- and NO_3^- will also oxidize I^- to I_2, so the test is not specific for these two reagents, and becomes positive for them only in the absence of the others. Thus Cu^{++}, Fe^{+3}, $Cr_2O_7^{--}$, etc., would all oxidize I^- to I_2, so in the presence of these the group test for ClO_3^- and NO_3^- would be of no value. Among the acid radicals included in the list in the present discussion, only AsO_4^{-3} is a strong enough oxidant to interfere. In the presence of AsO_4^{-3}, therefore, the individual tests must be tried directly.

6. Other reagents besides I^- may be used to test for the presence of oxidants in the solution. One that is frequently used is a solution of diphenylamine in concentrated H_2SO_4. To 1 cc. of the original solution add, with cooling, 1 cc. of concentrated H_2SO_4, and then a few drops of the reagent. The development of a blue color (by oxidation of the organic compound) is a fairly delicate test for an oxidant.

Test for Chlorate Ion

§287. **Manipulation.** — In the absence of Group II anions, place 2–3 cc. of the original solution in a test tube, acidify with HNO_3 if alkaline, adding 5 cc. excess, then add 1 cc. of $AgNO_3$ solution and 2 cc. of 0.5 *N* Na_2SO_3 solution. A white opalescence, changing promptly to a curdy, white precipitate indicates a chlorate.

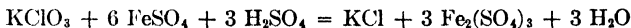
$$KClO_3 + AgNO_3 + 3\ Na_2SO_3 = \underline{AgCl} + KNO_3 + 3\ Na_2SO_4$$

§288. **Notes.** — 1. Since the test for ClO_3^- involves reduction to Cl^- and precipitation of the latter with $AgNO_3$, it is necessary to separate the ClO_3^- from Group II anions before the test can be applied. The simplest way to do this is to treat the original solution (after neutralizing if alkaline) with excess of $AgNO_3$. Silver chlorate is readily soluble, so the precipitate may be filtered out and the filtrate tested for ClO_3^-. First test the filtrate with more $AgNO_3$ to ensure completeness of precipitation of the halides, then add 5 cc. of 5 *N* HNO_3 and 1–2 cc. of 0.5 *N* Na_2SO_3. If ClO_3^- was present, AgCl will precipitate. The solution must not be acidified appreciably in carrying out this separation, otherwise the ClO_3^- may be lost by reaction with I^-.

2. In using Na_2SO_3 to reduce ClO_3^- to Cl^-, it should be remembered that Ag_2SO_3 will precipitate (white, granular) if too little HNO_3 is present, or if a large excess of Na_2SO_3 is added. In case difficulty is encountered due to failure to follow the directions properly in these respects, add 3–5 cc. more of HNO_3 and heat. Any Ag_2SO_3 will dissolve fairly readily, while AgCl will be unaffected. Sulfurous acid has some advantage over Na_2SO_3 in avoiding the error just mentioned, but a solution of H_2SO_3 is only moderately stable and is somewhat unpleasant to handle because of its strong odor. The difference between the two lies in the fact that Na_2SO_3 supplies SO_3^{--}, which combines with H^+ to form the slightly ionized HSO_3^-. Thus, if excess of a concentrated Na_2SO_3 solution were used, the HNO_3 might be neutralized sufficiently to permit precipitation of Ag_2SO_3.

3. An alternative reductant, in place of Na_2SO_3, is formaldehyde, CH_2O (5%–10% solution). This is a milder reductant than Na_2SO_3, but it avoids the precipitation of any compound other than AgCl. In using this reagent, adjust the conditions as described above, then add 2 cc. of CH_2O solution and heat to boiling. If ClO_3^- is present, a white precipitate of AgCl forms with reasonable promptness after the solution reaches the boiling point.

$$KClO_3 + 3\ CH_2O = KCl + 3\ CH_2O_2$$

4. Another reductant, intermediate between Na_2SO_3 and CH_2O in strength, is $FeSO_4$ [$FeSO_4 \cdot (NH_4)_2SO_4$ forms a more stable solution]. With moderate amounts of ClO_3^-, after preparing the solution as above and then adding 2–3 cc. of 0.2–0.3 *M* $FeSO_4$, the solution will become strongly opalescent, a precipitate separating slowly in the cold. With smaller quantities, it may be necessary to warm the solution slightly to obtain an immediate test.

$$KClO_3 + 6\ FeSO_4 + 3\ H_2SO_4 = KCl + 3\ Fe_2(SO_4)_3 + 3\ H_2O$$

5. In the test for ClO_3^-, it must be remembered that Cl^- is a common impurity in many reagents, therefore due care should be taken to try blank tests with the reagents to make sure that they are free from Cl^-, or contain so small an amount as to cause no serious interference.

Test for Nitrate Ion

§289. **Manipulation.** — In the absence of sulfide, iodide and bromide place 2 cc. of the original solution in a test tube, acidify with H_2SO_4 if alkaline, add 5 cc. of 0.2–0.3 *M* $FeSO_4$ solution, shake thoroughly, cool, and then, with the test tube inclined at an angle of approximately 60°, carefully pour in about 5 cc. of concentrated H_2SO_4. Cool under running water, and let stand a moment or two if necessary, for color to develop. A brown layer in the solution just above the concentrated H_2SO_4 indicates the presence of NO_3^-.

$$2\ HNO_3 + 8\ FeSO_4 + 3\ H_2SO_4 = 2FeSO_4 \cdot NO + 3\ Fe_2(SO_4)_3 + 4\ H_2O$$

§290. **Notes.** — 1. This test, known as the brown-ring test, depends upon the fact that $FeSO_4$, in the presence of concentrated H_2SO_4, will reduce NO_3^- to NO, and if excess of $FeSO_4$ is used, it will combine with the NO to form the somewhat unstable molecular compound to which the color is due. Occasionally, as a bottle of H_2SO_4 becomes nearly empty, it is found to have absorbed enough moisture from the air to be too dilute to give satisfactory results. In a similar way, a solution of $FeSO_4$ that has been standing for some weeks may have undergone sufficient oxidation by atmospheric oxygen to be unsuited for use. Such a reagent may be restored (Fe^{+3} reduced to Fe^{++}) by treating with a few cc. of H_2SO_4, adding metallic iron, warming, and letting stand 5–10 minutes. Then cool, filter (or decant), and return to the reagent bottle.

$$2\ Fe^{+3} + Fe^{\circ} = 3\ Fe^{++}$$

2. In pouring the H_2SO_4 into the test tube, care should be taken to let it run smoothly down the wall of the tube, with as little mixing as possible, to form a layer underneath the mixture of unknown and $FeSO_4$ solution. The readiness with which this may be done depends upon the considerable difference in density of the two solutions; concentrated H_2SO_4 having a density of 1.84, while that of the ordinary dilute aqueous solution seldom runs as high as 1.1. By using a pipette to transfer the H_2SO_4 to the test tube, the tip of the pipette can be placed in contact with the bottom of the test tube before letting the H_2SO_4 run in. In this way, an unusually sharp line can be established between the two layers; so sharp a line, in fact, that it may be necessary to swirl the solution slightly to form a more visible band of color.

3. Another favorite order of introducing the reagents consists in treating a portion of the original (or prepared) solution carefully with twice its volume of concentrated H_2SO_4, then cooling thoroughly, and pouring in carefully 4–5 cc. of $FeSO_4$ solution. The latter forms an upper layer in the test tube, and the brown color appears as usual between the two layers.

4. If ClO_3^- is present, this will use up part of the $FeSO_4$ so somewhat more of the latter reagent may be needed than was suggested above.

5. Both I^- and Br^- interfere seriously with the brown-ring test, due to liberation of I_2 and Br_2, which may be mistaken for the test for nitrate. In case either of these is present, it is best to precipitate the halides with excess of Ag_2SO_4 (free from NO_3^-), filter, and test the filtrate for NO_3^- by the brown-ring method. The chief objection to this procedure lies in the fact that a large volume of Ag_2SO_4 solution may be required (due to the slight solubility of Ag_2SO_4), so the solution may become fairly bulky by the time precipitation of the halides is complete. This decreases considerably the delicacy of the test if only a small portion of this solution is used; but by evaporating the solution to somewhere near its original volume, and then using all of the solution, or a large fraction of it, this difficulty can be overcome.

6. Another important test for a nitrate is the *ammonia* test. In this case, the NO_3^- is reduced with $NaOH + Al^\circ$ to NH_3 and identified by applying a test for the latter. The details of procedure are as follows: Place 2–3 cc. of the original solution in a test tube, add 5 cc. of 5 N NaOH, heat to boiling, and test for NH_3 with litmus paper. If the test is positive (showing the presence of NH_4^+ in the original solution), continue the heating until the test for NH_3 becomes negative. Then cool the solution somewhat, drop in a coil of heavy Al wire, insert a cotton plug in the mouth of the test tube (to hold back any spray from the alkaline solution), and lay a strip of moist red litmus paper over the mouth of the test tube. Heat the solution till the reaction is taking place vigorously at near 100°, then place the test tube in an inclined position in a beaker or test tube rack, and let the reaction run for 2–3 minutes. If a nitrate is present it will be reduced to NH_3, which will be carried out of the hot solution by the excess of H_2, turning the litmus paper blue.

$$3\ NaNO_3 + 8\ Al + 5\ NaOH + 2\ H_2O = 3\ NH_3 + 8\ NaAlO_2$$

In this test, aside from preliminary removal of NH_3, derived from NH_4^+, it is important to adjust the concentration of NaOH and the size of Al pieces in such a way that the reaction will be vigorous, but under control, at near 100°. At lower temperatures, the NH_3 distills out more slowly and is thus more highly diluted by the H_2. Since the NaOH reacts less readily with coarse Al wire than it does with spongy, granulated Al, it is possible to use higher concentrations of NaOH with the former than with the latter. If the reaction accelerates to the point of starting to froth up to the cotton plug, it may be slowed down again by slight cooling. If excessive cooling is required to keep the reaction under control, dilute the solution with a little water, or repeat the test using coarser, smooth Al°, or more dilute NaOH.

This test has the advantage that I^- and Br^- do not interfere, so it may well be substituted for the brown-ring test when these substances are present. If ClO_3^- is present, this will be reduced to Cl^- in the course of the reaction, so the NH_3 will be a little slower to appear, but there is no serious interference. Further, the procedure becomes a test for NO_3^- only because NH_4^+ and NO_3^- are the two forms of N being considered. If other forms of N were present, not removed by boiling with NaOH, but reduced to NH_3 by treatment with $NaOH + Al^\circ$, they would also give positive results in this test.

PART IV

SYSTEMATIC EXAMINATIONS

REMOVAL OF ORGANIC SUBSTANCES

§291. The methods of inorganic analysis do not provide against interference by organic compounds; and, in general, it is impossible to conduct inorganic analysis in material containing organic bodies. The removal of the latter can be effected, (1) by combustion at a red or white heat, with or without oxidizing reagents; (2) (in part), by oxidation with potassium chlorate and hydrochloric acid on the water bath (p. 200, 6′, 1); (3) by oxidation with nitric acid in presence of sulfuric acid, at a final temperature of the boiling point of the latter (p. 201, 2); (4) by solvents of certain classes of organic substances; (5) by dialysis. These operations are conducted as follows:

§292. *Combustion at a red or white heat,* of course, excludes analysis for mercury, arsenious and antimonous bodies (except as provided on p. 219), and ammonium. The last-named constituent can be identified from a portion of the material in presence of the organic matter (p. 424). If chlorides are present some iron will be lost at temperatures above 100°, and potassium and sodium waste notably at a white heat, and slightly at a full red heat. Certain acids will be expelled, and oxidizing agents reduced.

The material is thoroughly dried and then heated in a porcelain or platinum crucible, at first gently. It will blacken, by separation of the carbon of the organic compounds. The ignition is continued until the black color of the carbon has disappeared. In special cases of analysis, it is only necessary to char the material; then pulverize it, digest with the suitable solvents, and filter; but this method does not give assurance of full separation of all substances. Complete combustion, without use of oxidizing agents, is the way most secure against loss, and entailing least change of the material; it is, however, sometimes very slow. The operation may be hastened, with oxidation of all materials, by *addition of nitric acid, or of ammonium nitrate.* The material is first fully charred; then allowed to cool till the finger can be held on the crucible; enough nitric acid to moisten the mass is dropped from a glass rod upon it, and the heat of the water bath continued until the mass is dry, when it may be very gradually raised to full heat. This addition may be repeated as necessary. The ammonium nitrate may be added, as a solid, in the same way.

§293. *Oxidation with potassium chlorate and hydrochloric acid on the water bath* does not wholly remove organic matter, but so far disintegrates and changes it that the filtrate will give the group precipitates, pure enough

for most tests. It does not vaporize any bases but ammonium, but of course oxidizes or chlorinates all constituents. It is especially applicable to viscid liquids; it may be followed by evaporation to dryness and ignition, according to the paragraph above.

The material with about an equal portion of hydrochloric acid is warmed on the water bath, and a small portion of potassium chlorate is added at short intervals, stirring with a glass rod. This is continued until the mixture is wholly decolored and dissolved. It is then evaporated to remove chlorine, diluted and filtered. If potassium and chlorine are to be tested for, another portion may be treated with nitric acid on the water bath. The organic matter left from the action of the chlorine or the nitric acid may be sufficient to prevent the precipitation of aluminum and chromium in the third group of bases; so that a portion must be ignited. As to arsenic and antimony, see p. 219.

§294. The action of *sulfuric with nitric acid at a gradually increasing heat* leaves behind all the metals (not ammonium), with some loss of mercury and arsenic (and iron?) if chlorides are present in considerable quantity. In this, as in the operations before mentioned, volatile acids are lost — sulfides partly oxidized to sulfates, etc.

The substance is placed in a tubulated retort, with about four parts of concentrated sulfuric acid, and gently heated until dissolved or mixed. A funnel is now placed in the tubulure, and nitric acid added in small portions, gradually raising the heat, for about half an hour — so as to expel the chlorine, and not vaporize chlorides. The material is now transferred to a platinum dish and heated until the *sulfuric acid begins to vaporize*. Then add small portions of nitric acid, at intervals, until the liquid ceases to darken by digestion, after a portion of nitric acid is expelled. Finally, evaporate off the sulfuric acid, using the lowest possible heat at the close.

§295. *The solvents used* are chiefly *ether for fatty matter*, and alcohol or ether, or both successively, for resins. Instead of either of these, benzol may be used; and many fats and some resins may be dissolved in petroleum ether. It will be observed that ether dissolves some metallic chlorides, and that alcohol dissolves various metallic salts. Before the use of either of these solvents upon solid material, it should be thoroughly dried and pulverized. Fatty matter suspended in water solutions may be approximately removed by filtering through wet, close filters; also by shaking with ether or benzol, and decanting the solvent after its separation.

§296. *By dialysis*, the larger part of any ordinary inorganic substance can be extracted in approximate purity from the greater number of organic substances in water solution. The degree of purity of the separated substance depends upon the kind of organic material. Thus albuminoid

compounds are almost fully rejected; but saccharine compounds pass through the membrane quite as freely as some metallic salts. (Consult *Watts' Dictionary*, 1894, IV, 172.)

PRELIMINARY EXAMINATION OF SOLIDS

§297. Before proceeding to the analysis of a substance in the wet way, a careful study should usually be made of the reactions which the substance undergoes in the solid state, when subjected to a high heat, either alone or in the presence of certain reagents, before the blowpipe, or in the flame of the Bunsen burner. This examination in the dry way precedes that in the wet, and should be carried on systematically, following the plan laid down in the tables, and noting carefully every change which the substance under investigation undergoes, and if necessary making reference to some of the standard works on blowpipe analysis. In order to understand fully the nature of these reactions, the student should first acquaint himself with the character of the different parts of the flame, and the use of the blowpipe in producing the reducing and oxidizing flames.

§298. *The flame of the candle, or of the gas jet,* burning under ordinary circumstances, consists of three distinct parts: a dark nucleus or zone in the center, surrounding the wick, consisting of unburnt gas — a luminous cone surrounding this nucleus, consisting of the gases in a state of incomplete combustion. Exterior to this is a thin, non-luminous envelope, where, with a full supply of oxygen, complete combustion is taking place: here we find the hottest part of the flame. The non-luminous or outer part is called the **oxidizing flame**; the luminous part, consisting of carbon and unconsumed hydrocarbons, is called the **reducing flame.**

§299. *The flame produced by the blowpipe* (or Bunsen burner) is divided into two parts: the oxidizing flame, where there is an excess of oxygen, corresponding to the outer zone of the candle flame; and the reducing flame, where there is an excess of carbon, corresponding to the inner zone of the candle flame. Upon the student's skill in producing these flames depend very largely the results in the use of the blowpipe.

In order to produce a good **oxidizing flame,** the jet of the blowpipe is placed just within the flame, and a moderate blast applied — the air being thoroughly mixed with the gas, the inner blue flame, corresponding to the exterior part of the candle flame, is produced; the hottest and most effective part is just before the apex of the blue cone, where combustion is most complete.

The **reducing flame** is produced by placing the blowpipe just at the edge of the flame, a little above the slit, and directing the blast of air a

little higher than for the oxidizing flame. The flame assumes the shape of a luminous cone, surrounded by a pale-blue mantle; the most active part of the flame is somewhat beyond the apex of the luminous cone.

§300. The blast with the blowpipe is not produced by the lungs, but by the action of the muscles of the cheek alone. In order to obtain a better knowledge of the management of the flame, and to practice in producing a good reducing flame, it is well to fuse a small grain of metallic tin upon charcoal, and raising to a high heat endeavor to prevent its oxidation, and keep its surface bright; or better, perhaps, to dissolve a speck of manganese dioxide in the borax bead on platinum wire — the bead becoming amethyst red in the outer flame and colorless in the reducing flame. The beginner should work only with substances of a known composition, and not attempt the analysis of unknown complex substances, until he has made himself perfectly familiar with the reactions of at least the more frequently occurring elements.

The amount of substance taken for analysis should not be too large; a quantity of about the bulk of a mustard seed being, in most cases, quite sufficient.

The physical properties of the substance under examination are to be first noted; such as color, structure, odor, luster, density, etc.

Heat in Glass Tube Closed at One End

§301. The substance, in fragments or in the form of a powder, is introduced into a small glass tube, sealed at one end, or into a small matrass, and heat applied gently, gradually raising it to redness, if necessary with the aid of the blowpipe. When the substance is in the form of a powder it is more easily introduced into the tube by placing the powder in a narrow strip of paper, folded lengthwise in the shape of a trough; the paper is now inserted into the tube held horizontally, the whole brought to a vertical position, and the paper withdrawn; in this way the powder is all deposited at the bottom of the tube. By this treatment in the glass tube we are first to notice whether the substance undergoes a change, and whether this change occurs with or without decomposition. The sublimates, which may be formed in the upper part of the tube, are especially to be noted. Escaping gases or vapors should be tested as to their alkalinity or acidity, by small strips of moist red and blue litmus paper inserted in the neck of the tube.

Heat in Glass Tube Open at Both Ends

§302. The substance is inserted into a glass tube from two to three inches long, about one inch from the end, at which point a bend is sometimes made;

heat is applied gently at first, the force of the air current passing through the tube being regulated by inclining the tube at different angles. Many substances undergoing no change in the closed tube absorb oxygen and yield volatile acids or metallic oxides. As in the previous case, the nature of the sublimate and the odor of the escaping gas are particularly to be noted. The reactions of sulfur, arsenic, antimony and selenium are very characteristic; these metals, if present, are generally easily detected in this way (p. 208–9).

Heat in Blowpipe Flame on Charcoal

§**303**. For this test, a well-burned piece of charcoal is selected, and a small cavity made in that side of the coal showing the annular rings; a small fragment of the substance is placed in the cavity, and, if the substance be a powder, it may be moistened with a drop of water. The coal is held horizontally, and the flame made to play upon the assay at an angle of about twenty-five degrees. The substance is brought to a moderate heat, and finally to intense ignition. Any escaping gases are to be tested for their odor; the change of color which the substance undergoes, and the nature and color of the coating which may form near the assay, are also to be carefully noted. Some substances, as lead, may be detected at once by the nature of the coating.

Ignition of the Substance previously Moistened with a Drop of Cobalt Nitrate

§**304**. This test may be effected either by heating on charcoal, in the loop of platinum wire, or in the platinum-pointed forceps. A portion of the substance is moistened with a drop of the reagent, and exposed to the action of the outer flame. When the substance is in fragments, and porous enough to absorb the cobalt solution, it may be held in the platinum-pointed forceps and ignited. The color is to be noted after fusion. This test is rather limited; aluminum, zinc and magnesium giving the most characteristic reactions.

Fusion with Sodium Carbonate on Charcoal

§**305**. The powdered substance to be tested is mixed with sodium carbonate, moistened and placed in the cavity of the coal. Some substances form, with sodium carbonate at a high heat, fusible compounds; others infusible. Many bodies, as silicates, require fusion with alkali carbonate before they can be tested in the wet way. Many metallic oxides are reduced to metal, forming globules, which may be easily detected.

When this test is applied for the detection of sulfates and sulfides, the flame of the alcohol lamp is to be substituted for that of the gas flame, as the latter generally contains sulfur compounds.

Examination of the Color which may be imparted to the Outer Flame

§306. In this way many substances may be definitely detected. The test may be applied either on charcoal or on the loop of platinum wire, preferably in the latter way. When the substance will admit, a small fragment is placed in the loop of the platinum wire, or held in the platinum-pointed forceps, and the point of the blue flame directed upon it. If the substance is in a powder it may be made into a paste with a drop of water, and placed in the cavity of the charcoal, the flame being directed horizontally across the coal. The color which the substance imparts to the outer flame in either case is noted. In most cases the flame of the Bunsen burner alone will suffice; the substance being heated in the loop of platinum wire, which, in all cases, should be first dipped in hydrochloric acid and ignited, in order to secure against the presence of foreign substances. Those salts which are more volatile at the temperature of the flame, as a rule give the most intense coloration. When two or more substances are found together it is sometimes the case that one of them masks the color of all the others; the bright yellow flame of sodium, when present in excess, generally veiling the flame of the other elements. In order to obviate this, colored media, as cobalt-blue glass, indigo solution, etc., are interposed between the flame and the eye of the observer. The appearance of the flame of various bodies, when viewed through these media, enables us often to detect very small quantities of them in the presence of large quantities of other substances.

Treatment of the Substance with Borax and Microcosmic Salt

§307. This is best effected in the loop of platinum wire. This is heated and dipped into the borax or microcosmic salt and heated to a colorless bead; a small quantity of the substance under examination is now brought in contact with the hot bead, and heated, in both the oxidizing and reducing flames. Any reaction which takes place during the heating must be noticed; most of the metallic oxides are dissolved in the bead, and form a colored glass, the color of which is to be observed, while hot and while cold. The color of the bead varies in intensity, according to the amount of the substance used; a very small quantity will, in most cases, suffice. Certain bodies, as the alkaline earths, dissolve in borax, forming beads which, up to a certain degree of saturation, are clear. When these beads are brought

into the reducing flame, and an intermittent blast used, they become opaque. This operation is called **flaming.**

As reducing agents, certain metals are employed in the bead of borax or microcosmic salt. For this purpose **tin** is generally chosen, *lead* and *silver* being taken in some cases. These metals cannot be used in the loop of platinum wire, as they will alloy the platinum. The beads are first formed in the loop of wire; then, while hot, shaken off into a porcelain dish, several being so obtained. A number of these are now taken on charcoal and fused into a large bead, which is charged with the substance to be tested, and then, with the tin or other metal. For this purpose tin foil (or lead foil) is previously cut in strips half an inch wide, and the strips rolled into rods. The end of the rod is touched to the hot bead to obtain as much of the metal as required. Lead may be added as precipitated lead ("proof-lead"), and silver as precipitated silver. By aid of tin in the bead, cuprous oxide, ferrous oxide and metallic antimony are obtained and other reductions effected, as directed on p. 258, and elsewhere.

§308. Preliminary examination of solids

Note physical properties, such as Structure, Gravity, Color, Odor, etc.

I. Heat a portion, finely pulverized in a Dry Glass Tube closed at one end (§301).

1. *The substance suffers no change:*
   Absence of volatile bodies (including combined water), of organic compounds, and of those which change color on heating.

2. *The substance changes color:*
   Organic compounds *blacken* from separation of carbon, which burns.
   Cu and **Co** salts *blacken* at high heat.
   ZnO and most **Zn** salts, *yellow while hot, white when cold.*
   PbO and **Pb** salts, *yellow while hot, yellow when cold.*
   Bi_2O_3 (white) and many **Bi** salts, *orange to red brown while hot, pale yellow when cold.*
   Fe_2O_3, and salts, *red to black while hot, reddish brown when cold.*
   $Cd(OH)_2$ and many **Cd** salts, *brown while hot, brown when cold.*
   SnO_2, *brown while hot, yellow when cold.*

3. *The substance fuses:*
   Most **alkali salts** and numerous other salts. Many salts dissolve in their water of crystallization when heated, becoming solid again by vaporization.

4. *The substance sublimes*, partially or wholly:
   H_2O of crystallization, combination, or absorption.
   Sublimate condensing in cold part of the tube.
   Hg (p. 171), *gray*, easily rubbed to globules.
   $HgCl_2$ first melts, then forms *white* crystalline sublimate.
   Hg_2Cl_2, without melting, forms a sublimate, *yellow while hot, white when cold.*
   HgS, a *black* sublimate, turning red on trituration.
   As, *steel-gray* sublimate; *garlic odor.*
   As_2O_3 sublimes in *white* octahedral crystals, does not fuse (p. 208).
   As_2S_3, sublimate nearly *black while hot, reddish yellow when cold.*
   Sb_2S_3 fuses yellow; forms *white*, amorphous sublimates.

NH_4 salts, those not decomposing, *white* sublimate (p. 426).
$FeCl_3$ slowly sublimes as a reddish-yellow stain (p. 322).
S, free or by reduction of sulfide, gives reddish-brown drops, yellow when solidified.
$H_2C_2O_4$, a heavy white vapor and *crystalline* sublimate.
I, a violet vapor and *blue-black* sublimate.

5. *The substance evolves a gas or vapor:*
   O indicates the presence of a **nitrate, chlorate, bromate, iodate** or **peroxide. A** small piece of coal placed upon the assay glows upon being heated.
   H_2S, from hydrated **sulfides** and some **sulfites,** blackens *lead-paper.* Recognized by its *odor.* Poisonous.
   SO_2, from **sulfites, thiosulfates,** certain **sulfates,** etc. Recognized by its odor and bleaching effect.
   NH_3, from its compounds which decompose, *characteristic odor,* and alkaline *reaction on litmus.*
   CN, recognized by characteristic *odor* and violet *flame.* Intensely poisonous.
   Oxides of Nitrogen, from **nitrates** or **nitrites,** *reddish brown, acrid vapor.*
   Acetone, from **acetates,** characteristic *fragrant odor.*

II. Heat in a Glass Tube open at both ends (§302).

Certain of the changes stated above as occurring in operation I are modified by **oxidation:**
Metals form oxides, except **Ag, Au** and **Pt.**
S and **sulfides** yield SO_2. Recognized by its odor and action on litmus paper.
As yields a sublimate of As_2O_3.
Sb yields a sublimate (white) of Sb_2O_3 and Sb_2O_5.
Bi, a sublimate, dark brown while hot, lemon yellow when cold (Bi_2O_3).
Te, gray sublimate of **tellurous anhydride** (TeO_2).
Se and **selenides** evolve SeO_2, odor resembling that of rotten horse-radish (p. 300).
Hg, sublimate of metallic mercury.

III. Heat in the Blowpipe Flame on Charcoal (§303).

1. *The substance decrepitates:*
   Crystals as **NaCl.** (If finely pulverized, the decrepitation is avoided.)

2. *The substance deflagrates:*
   Nitrates, Chlorates, Iodates, Hypophosphites, Permanganates, etc.

(*Continued on page* 588)

3. *The substance fuses, and is absorbed by the charcoal:*
   Salts of alkalis and some salts of alkaline earths.

4. *The substance is infusible and incandescent:*
   Ba, Sr, Ca, Mg, the residue is alkaline to test paper.
   Al_2O_3, MgO, ZnO (yellow while hot), not alkaline to test paper.

5. *The substance forms an incrustation on charcoal:*
   Pb, *lemon yellow while hot,* sulfur yellow when cold. In thin layers, **bluish white, volatile** with bluish flame.
   Bi, dark *orange yellow while hot,* lemon yellow when cold.
   Zn, *yellow while hot,* white when cold, greenish-white flame.
   Cd, *red brown,* volatile, dark-yellow flame.
   As, *white.* Readily volatilized, **distant from the assay, faint blue flame.**
   Sb, *white,* pale-green flame.
   Sn, *faint yellow while hot,* white when cold.

IV. The Substance (or incrustation of Test III, 5) **is moistened with solution of Cobalt Nitrate and strongly ignited (§304).**

1. *The mass or incrustation is colored:*
   ZnO, *yellowish green.*
   SnO, *bluish green.*
   Sb_2O_5, *dirty dark green.*
   Al_2O_3, SiO_2, phosphates, ***blue.***
   MgO, *flesh color* or *pink.*
   BaO, *brick red.*
   SrO, CaO, *gray.*

V. Heat with Na_2CO_3, on charcoal in the inner Blowpipe Flame (§305).

1. *Metallic grains are obtained:*
   Bi, Sb, *brittle.*
   Pb, Cu, Sn, Au, *malleable.*

2. *An infusible magnetic powder is obtained:*
   Fe, Ni, Co.

VI. Heated in the Blowpipe Flame, or in the Bunsen Flame on Charcoal, or in a loop of Platinum Wire (§306).

1. *The substance colors the outer flame:*

(If Test V. does not reduce metal, heat *on platinum wire* **for flame color, before the blowpipe** or in Bunsen flame.)

Yellow: **Na** and its salts, even in small quantities, impart an intense reddish yellow.
Other salts, even in large quantities, do not interfere with this reaction; viewed through a green glass, appears orange yellow; moistened with sulfuric acid, the test is more delicate (p. 422).

Violet: **K** and most of its salts, except borates, phosphates and silicates, give bluish-violet flame, distinguished in presence of very small quantities of sodium compounds. Excess of the latter prevents the reaction; **Li** also masks the reaction. In presence of sodium, the potassium flame appears reddish violet when viewed through a blue glass (p. 420).

Red: **Ca** and its compounds produce a yellowish-red flame (p. 407).
Sr and many of its salts yield a crimson flame, masked by much **Ba** (p. 403).
Li and its salts produce a carmine-red flame (p. 431). Sodium interferes with the reaction; potassium does not.

Green: Yellowish green, **Ba** and most of its salts. Also, **Mo** and its compounds.
Emerald green, **Cu** and most of its compounds.
Bluish green, B_2O_3.
Yellowish green, B_2O_3, best obtained by the addition of sulfuric acid. Heat on platinum wire until the sulfuric acid is expelled, then moisten with glycerine and ignite (p. 443).
Whitish green, **Zn.**

Blue: Light blue, **As** and many arsenic compounds.
Azure blue, **Pb, Se.** Also, $CuCl_2$.
Greenish blue, **Sb**, $CuBr_2$.

§309. Behavior of Substances before the blowpipe with Microcosmic salt and borax. A clear bead is formed by fusing the flux on a loop of platinum wire. Dip the bead in the finely powdered substance to be examined, and heat again — first in the oxidizing flame; second in the reducing or inner flame. Metallic salts are mostly changed to oxides. In the Table *h.*, signifies hot; *c.*, cold; *sups.*, supersaturated with oxide; **s. s.**, strongly saturated; *h. c.*, hot and cold.

Color of the Bead	With Microcosmic Salt, Sodium Ammonium Hydrogen Phosphate		With Sodium Tetraborate (Borax)	
	In outer or oxidizing Flame	*In inner or reducing Flame*	*In outer or oxidizing Flame*	*In inner or reducing Flame*
Colorless	Si (swims undissolved) **Al, Mg, Ca, Sr, Ba, Sn** (*s. s., opaque*) **Ti, Zn, Cd, Pb, Bi, Sb** (*not sat.*)	Si (swims undissolved) **Al, Mg, Ca, Sr, Ba** (*sups. not clear*) **Ce, Mn, Sn**	*h. c.*: **Si, Al, Sn** (*sups. opaque*) **Al, Mg, Sr, Ca, Ba, Ag** (*not sat.*) **Zn, Cd, Pb, Bi, Sb, Ti, Mo**	**Si, Al, Sn** (*s. s. opaque*) Alkaline earths and earths *h. c.*: **Mn, Ce** *h.*: **Cu**
Yellow or Brownish	*h.* (*s. s.*): **Fe, U, Ce** *c.*: **Ni**	*h.*: **Fe, Ti** *c.*: **Ni**	*h.*, *not sat.*: **Fe, U** *h.*, *sups.*: **Pb, Bi, Sb**	*h.*: **Ti, Mo**
Red	*h.* (*s. s.*): **Fe, Ni, Cr, Ce**	*c.*: **Cu** *h.*: **Ni, Ti** with **Fe**	*h.*: **Fe, Ce** *c.*: **Ni**	*c.*: **Cu** (*sups. opaque*)
Violet or Amethyst	*h. c.*: **Mn**	*c.*: **Ti**	*h. c.*: **Mn** *h.*: **Ni** with **Co**	*c.*: **Ti**
Blue	*h. c.*: **Co** *c.*: **Cu**	*h. c.*: **Co** *c.*: **W**	*h. c.*: **Co** *c.*: **Cu**	*h. c.*: **Co**
Green	*h.*: **Cu, Mo; Fe** with **Co** or **Cu** *c.*: **Cr**	*c.*: **Cr** *h.*: **U, Mo**	*c.*: **Cr** *h.*: **Cu, Fe** with **Co**	**Cr** *sups.*: **Fe**
Gray and Opaque		**Ag, Pb, Sb, Cd, Bi, Zn, Ni**		The same as with microcosmic salt

THE ANALYSIS OF DRY UNKNOWNS

The discussion of dry unknowns will be limited to the ordinary free and combined forms of the metals and non-metals whose methods of identification are presented in detail in Parts II and III of this book. This provides ample material to illustrate the problems involved in dealing with dry substances, and covers all that one has time to touch on in completing the usual introductory course.

§**310**. *Simple and Complex Dry Unknowns.* — It is convenient to divide the study of dry unknowns into two parts. The first covers relatively simple materials, such as an individual metal, alloy, oxide, hydroxide, normal-, acid-, or basic-salt, or double salt. In this case the material may be dissolved in water, or with the aid of acids or special reagents, and tests applied by which the substance may be identified. From these studies it should be possible to assign a formula or name to the unknown with reasonable certainty. The second part of the study of dry unknowns covers complex mixtures of the above simple materials. In such a case the ordinary chemical examination is not sufficient, usually, to determine the individual substances present in the original mixture. Even in the treatment with water, reactions may take place such that the composition is distinctly changed, and it may not be possible to decide how the various metals and acid radicals were combined at the start. Occasionally, when the individual substances in the mixture are left in rather coarse form, they may be sorted out and examined separately. With a powdered mixture, however, such a process would be very laborious at best. It may be noted that other tools are available, such as examination with the microscope, spectrograph, or X-ray photograph, by which the components of the mixture may be identified. Such methods supplement in a very important way the ordinary chemical examination of materials, but special training is required before they can be applied. In spite of the limitations of chemical analysis, it is possible to use a somewhat artificial approach to the study of these complex mixtures and obtain important practice in the collection of pertinent facts. Further, the interpretation of these facts, in the sense of setting up a chemical picture that will be consistent with them, provides a situation typical of most chemical problems.

THE STUDY OF SIMPLE MATERIALS

§**311**. *Preliminary Tests with Solvents.* — If the material is in coarse pieces, it should be reduced to a finely divided state if possible, so as to increase the rate of its reaction with the various solvents. Then place about 0.05 g. portions in each of several test tubes and try the action separately of water, 5 N HCl, 5 N HNO_3, and HCl + HNO_3 (3 vols. of

5 *N* HCl to 1 vol. of 5 *N* HNO_3). In doing this, add 5–10 cc. of the solvent, look for evidences of reaction, heat if necessary, and continue the operation until the reaction has gone as far as it will; either dissolving the dry completely, or leaving a residue which is obviously not being acted upon further. During the process of dissolving, it is important to look for evidences of reactions occurring by which materials may be lost which will need to be identified when the regular sample is being dissolved for analysis.

§**312**. *Reactions Occurring in the Dissolving Process.* — On treatment with water, the chief reactions that may occur are hydrolysis and decomposition (as the solution is heated). Thus, many of the normal salts react with water to form basic salts which may precipitate to a greater or less extent, while the aqueous solution becomes acid. Or, acid salts may be formed (which are generally soluble), the aqueous solution becoming alkaline. Typical salts to illustrate these cases are $BiCl_3$ and Na_2CO_3. The former, on treatment with water, yields a copious precipitate of BiOCl, and a solution containing HCl and small amounts of $BiCl_3$. Sodium carbonate, on the other hand, dissolves readily and completely in water, but the resulting solution is alkaline. In some cases, if the solution is heated, gases may form which need to be identified. Thus $NaHCO_3$, on being dissolved in hot water, is largely decomposed into Na_2CO_3, H_2O and CO_2. Examination of the resulting solution would not be sufficient to identify $NaHCO_3$ as distinct from Na_2CO_3, in fact, the solution would contain Na_2CO_3 and not $NaHCO_3$. But the facts that CO_2 was given off (and identified) and sodium and carbonate ions were identified in the water solution, would be reasonable grounds for reporting the substance as $NaHCO_3$. In extreme cases, certain constituents may be lost completely if the heating be prolonged. Thus, ammonium carbonate (the commercial salt is a mixture of NH_4HCO_3 and $NH_4NH_2CO_2$), on dissolving in water and boiling, is completely decomposed into NH_3 and CO_2; and Al_2S_3, prepared in the dry way, is completely hydrolyzed into $Al(OH)_3$ and H_2S, the latter being driven off as a gas on boiling. Still another possible reaction on treatment with water is seen in the case of metallic calcium, $Ca + 2\,H_2O = Ca(OH)_2 + H_2$.

On treatment with HCl, various reactions may occur, most of which may be recognized through identification of reaction products. The four most common cases involve the evolution of gases; H_2, CO_2, H_2S and Cl_2. (*a*) The more electropositive metals dissolve in HCl with evolution of H_2. There is no direct test by which the H_2 can be easily identified, though if tests for CO_2 and H_2S are negative, it may be assumed that any effervescence is due to H_2. Further, it may be recalled that, while H_2 is odorless, the presence of certain impurities in the ordinary metals (C, S, P) may cause the gas as actually evolved to have a pronounced, rather unpleasant odor. This is sufficiently characteristic to serve as an important

indirect test for H_2. (It may be experienced easily by treating Fe° or Zn° with dilute HCl, warming until the reaction is proceeding briskly, and then noting the odor.) (*b*) Carbonates react with HCl with evolution of CO_2. This usually takes place in the cold, though certain of the basic carbonates require heating before ready action occurs. The CO_2 may be identified with the aid of lime water, either bubbling the gases into lime water, or dipping a glass rod into lime water and then holding it just above the surface of the liquid so that any CO_2 coming off may turn the film of $Ca(OH)_2$ solution milky, $Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$. (*c*) Many sulfides react with HCl with liberation of H_2S. This is a colorless gas of pronounced odor. (Caution! H_2S is very poisonous!) It is identified by testing the fumes above the solution with lead acetate paper (a strip of filter paper moistened with $Pb(C_2H_3O_2)_2$ solution). If H_2S is present, a black stain of PbS will appear on the test paper. (*d*) Strong oxidants react with HCl with formation of Cl_2. Thus, MnO_2 forms $MnCl_2$, Cl_2 and H_2O; also $BaCrO_4$, on heating with excess of HCl, is converted to $BaCl_2$, Cl_2, $CrCl_3$ and H_2O. Since Cl_2 is itself a fairly strong oxidant, it is possible to test for the presence of an oxidant in the gases escaping from the solution, and if one is found it may be assumed to be Cl_2, derived from the oxidation of the HCl. The test is applied with potassium iodide paper (a strip of filter paper moistened with KI solution). Any Cl_2 present will react with the KI, setting I_2 free, and producing a brown stain on the test paper.

On treatment with HNO_3, the chief reactions to be recognized are formation of CO_2 from carbonates, as in the case of HCl, and reduction of the HNO_3 by some reductant. The procedure for identification of CO_2 is given under HCl, above. Possibility of recognizing the reduction of HNO_3 depends upon the fact that as nitric acid is reduced during its ordinary employment as a solvent, the nitrate ion undergoes decomposition, forming NO, among other products. The nitric oxide combines with oxygen from the air to form N_2O_4, which is brown in color. Thus the appearance of brown fumes as the substance dissolves in HNO_3 may be taken as evidence of a reductant being present. There are, of course, many reductants capable of producing this effect. Free metals, sulfites, sulfides, iodides, bromides, and even chlorides, and compounds of Sn, Fe, Cu, As, Sb and Hg exhibiting the lower valences of these metals are oxidized with varying degrees of readiness by HNO_3. Occasionally other reaction products may be identified, such as free sulfur, from sulfides, and free iodine, from iodides; but frequently one needs to depend upon additional tests and observations on the original material to distinguish between certain possibilities. Thus, powdered Fe, FeO and Fe_3O_4, are all black, and all dissolve in HNO_3 with evolution of brown fumes; but if the reactions with HCl are observed, Fe dissolves with evolution of H_2, FeO dissolves without evolution of H_2, forming a solution of $FeCl_2$, and Fe_3O_4 dissolves without evolution of H_2, forming a solution containing 2 parts of $FeCl_3$ to 1 of

$FeCl_2$. Of the reaction products which may be recognized when HNO_3 is being reduced, sulfur usually separates in the dark, rubbery form, which may be removed from the solution with a glass rod, rinsed thoroughly, and burned, noting the characteristic odor of SO_2. Iodine forms violet-colored vapors as it volatilizes from the hot solution. If there is only a small amount of iodine given off it may be overlooked, and so special procedures might be needed to recover this and identify it; but the simple unknowns being considered at this point should cause no trouble.

When nitrohydrochloric acid is used as the solvent, CO_2 will be evolved from carbonates, just as in the cases of HCl and of HNO_3 used separately. Beyond this there is relatively little further information to be obtained. Certain oxidants, such as MnO_2, may be reduced by the HCl present, but since the HCl and HNO_3 react with each other when heated, one cannot use the test for Cl_2 to identify the substance as an oxidant. In the same way, certain reductants may undergo oxidation, but one cannot always recognize this reaction through the brown fumes given off, because this same effect may be obtained on heating the reagent itself. In the cases of sulfides and iodides, S° and I_2 may be obtained which are identified as indicated under HNO_3, above. Further, some of the S° may be oxidized to H_2SO_4, giving a test for sulfate radical in the acid solution. In the same way, some of the I_2 may be oxidized to HIO_3, from which the I_2 may be liberated again by the use of $FeSO_4$ (identifying the I_2 as usual with CCl_4), $2\ HIO_3 + 10\ FeSO_4 + 5\ H_2SO_4 = 5\ Fe_2(SO_4)_3 + I_2 + 6\ H_2O$.

Thus it will be seen that important tests and observations are to be made during the dissolving of the substance in acids, which may help materially in deciding the composition of the original unknown. Further, it will be noted that the process of dissolving in HCl + HNO_3 yields less supplementary information than when the separate acids are used.

§**314**. *Special Methods for Substances Insoluble in Acids.* — In the preliminary study of the behavior of the substance with the various acids, it may appear that none of them are particularly effective. This may be due to the fact that the reaction is taking place slowly, or that the material is at best only slightly soluble in the given solvent. Thus metallic chromium, nickel oxide, and some of the amalgams running high in mercury, react very slowly with the 5 N acids. In such cases it is usually worth while to try the effect of the stronger acids. For this purpose, HCl may be used directly in the concentrated form (approximately 11.5 N), concentrated HNO_3 is usually diluted with its own volume or with half its volume of water (1–1 HNO_3 = 8 N, 2–1 HNO_3 = 10.6 N), and the HCl-HNO_3 reagent is usually made up with about equal volumes of 11.5 N HCl and 5 N HNO_3. If the reaction starts fairly readily with these reagents, it may be simplest to see that the material is well powdered and then let it digest as long as is necessary, with occasional shaking, until the material dissolves.

In other cases, such as $BaSO_4$, AgBr and ignited SnO_2, the material is so insoluble in the acids, or reacts so slowly with them, that it becomes necessary to consider special methods of treatment that may be employed. These may serve either to dissolve the substance directly, or to convert it to products that can be dissolved readily by the use of the conventional solvents. Typical materials that may require such treatment are silver halides, sulfates of Ba, Sr, Ca and Pb, fused $PbCrO_4$ (used as an oxidizer in certain organic combustions), and several oxides that have been heated at high temperatures (so-called ignited oxides) or that occur in nature, especially SnO_2, Cr_2O_3, Al_2O_3 and Fe_2O_3. Occasionally special reagents may be tried as individual solvents for certain of these compounds. Ammonium hydroxide (5 *N* or stronger) is a fairly effective solvent for AgCl, and slightly less so for AgBr. Concentrated sodium acetate (3 *N* or stronger) is useful to dissolve $PbSO_4$. A procedure that is more general in its application depends upon the readiness with which silver halides react with metallic Zn in the presence of dilute H_2SO_4. Place a little of the material in a test tube, cover with water, add 1 cc. of 5 *N* H_2SO_4 and 0.3–0.5 g. of Zn°, warm and let stand a few minutes with occasional shaking. The silver halide is reduced to metallic Ag, the halogen going into solution as halide ion. Filter and wash. The filtrate may be tested for the halide ion, the residue (Zn° + Ag°) may be dissolved in HNO_3 and the tests for Ag^+ applied. A procedure, similar in principle, may be used in the case of the insoluble sulfates, to separate the metal from the radical with which it forms the insoluble compound. Transfer a portion of the material to a beaker or casserole, add 15–20 cc. of 3 *N* Na_2CO_3 solution (free from SO_4^{--}) and heat to boiling, letting the reaction continue at 95°–100° for several minutes. The sulfates are transposed by this treatment into carbonates, which remain precipitated and look much like the sulfates originally present. The sulfate radical has gone into solution, however. Filter, wash, test the filtrate for SO_4^{--}, and dissolve the precipitate in HNO_3 or $HC_2H_3O_2$ to test for the metal that was associated with the sulfate radical originally. In the case of $BaSO_4$, the conversion to $BaCO_3$ by this procedure is somewhat incomplete. If an appreciable amount of $BaSO_4$ is left unacted upon, this will fail to dissolve in the acid later. In this case, transfer the precipitate to the casserole and treat again with Na_2CO_3. Two treatments in this way will take care of ordinary quantities of $BaSO_4$.

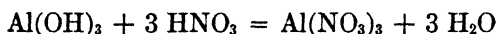
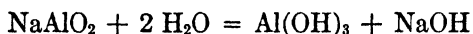
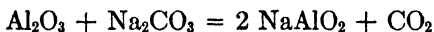
The next types of procedure to be mentioned are fusion or ignition methods. The most common of these is fusion with alkali carbonate (Na_2CO_3 or K_2CO_3; frequently a mixture of the two in equimolar proportions, a reagent which melts at a lower temperature than either of the compounds separately). In this case 0.3–0.5 g. of the dry, powdered material is thoroughly mixed with 3–5 g. of the dry reagent, the mixture being placed in a nickel crucible (platinum or silver crucibles are also used), and heated with the full Bunsen flame until the alkali carbonate melts.

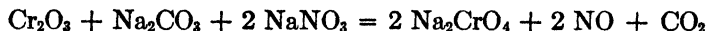
(If the crucible is large, a larger flame may be required.) The mass is kept in a fused state for 15–20 minutes to allow reasonable time for the various reactions to take place. It is then permitted to cool thoroughly. Place the crucible on its side in a beaker or casserole, cover with water, heat to boiling, and let digest, hot, until the fusion mass is thoroughly disintegrated. Filter, wash, reserve the filtrate to test for certain constituents, dissolve the residue in HNO_3 and analyze this solution for metals.

Fusion with alkali carbonate is an effective treatment for all of the materials listed above, except SnO_2. Silver halides are converted to metallic silver and alkali halide, the latter going into solution with water, while the Ag is soluble in HNO_3. $4\ AgI + 2\ Na_2CO_3 = 4\ Ag^\circ + 4\ NaI + 2\ CO_2 + O_2$. Fused lead chromate and the insoluble sulfates are transposed to carbonates and alkali chromate or sulfate, the latter dissolving in water, while the carbonates are soluble in HNO_3. $SrSO_4 + Na_2CO_3 = SrCO_3 + Na_2SO_4$. The ignited oxides of Al, Fe and Cr, are converted to aluminate, ferrite and chromite, which are hydrolyzed by the water with precipitation of the hydroxides, the latter dissolving readily in HNO_3 (or HCl).

$$Al_2O_3 + Na_2CO_3 = 2\ NaAlO_2 + CO_2$$

$$NaAlO_2 + 2\ H_2O = Al(OH)_3 + NaOH$$

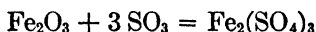
$$Al(OH)_3 + 3\ HNO_3 = Al(NO_3)_3 + 3\ H_2O$$

In the case of $NaAlO_2$, precipitation of the hydroxide may be incomplete, some of the Al staying in solution in the form of AlO_2^-. This may be found by proper examination of the aqueous extract. With Fe, the material precipitates completely as the hydroxide on digesting the fused product with H_2O. During the process of fusion, Cr behaves somewhat differently than Al and Fe. Due to the readiness with which Cr^{III} is oxidized to Cr^{VI} in an alkaline medium, the molten mass absorbs oxygen from the air to oxidize part of the Cr to a chromate. $Cr_2O_3 + 2\ Na_2CO_3 + 3\ O_2 = 2\ Na_2CrO_4 + 2\ CO_2$. If the oxidation is complete, the Na_2CrO_4 will be found in the water extract; if the oxidation is incomplete, the Cr may precipitate largely as chromic chromate, $Cr_2(CrO_4)_3$, red brown in color, soluble in HNO_3. In case Cr is suspected, due to its somewhat characteristic green color, it is common practice to modify the fusion mixture by adding a small amount of nitrate or chlorate to supply an oxidant within the solution itself to ensure complete oxidation of the Cr.

$$Cr_2O_3 + Na_2CO_3 + 2\ NaNO_3 = 2\ Na_2CrO_4 + 2\ NO + CO_2$$

It will be noted that the procedures suggested take care of all the cases listed except that of SnO_2. Several special methods are available for the effective handling of this compound. One is fusion in a nickel crucible

with solid KOH, the SnO_2 being converted to K_2SnO_3. On cooling, the mass may be dissolved in water and the usual tests applied. Another method frequently employed in analytical work, uses a mixture of dry Na_2CO_3 and S°. These materials are thoroughly mixed with the SnO_2, placed in a porcelain crucible and carefully heated at approximately 400° (well below a red heat) for 15–20 minutes. The excess sulfur volatilizes and catches fire from the flame. The reaction involved in this ignition is the conversion of SnO_2 to Na_2SnS_3, $2\ SnO_2 + 2\ Na_2CO_3 + 9\ S = 2\ Na_2SnS_3 + 3\ SO_2 + 2\ CO_2$. Cool, extract with water, which dissolves the Na_2SnS_3, acidify with dilute HCl, precipitating SnS_2, and complete the tests for Sn as in the Arsenic division of Group II. A third method occasionally used to convert the SnO_2 into a soluble material consists in fusing with KCN in a porcelain crucible. This reduces the SnO_2 to Sn°, which is soluble in HCl or $HCl + HNO_3$. $SnO_2 + 2\ KCN = Sn° + 2\ KCNO$.

Sodium carbonate is an alkaline fusion reagent. It is possible to carry out certain fusion reactions with the aid of an acid fusion reagent. The one most commonly used for this purpose is sodium pyrosulfate, $Na_2S_2O_7$ (prepared from $NaHSO_4$ by careful heating, $2\ NaHSO_4 = Na_2S_2O_7 + H_2O$). This reagent is effective in the treatment of small amounts of basic oxides, due to its decomposition to yield SO_3 which combines with the basic oxide to form a sulfate.

$$Na_2S_2O_7 = Na_2SO_4 + SO_3$$

$$Fe_2O_3 + 3\ SO_3 = Fe_2(SO_4)_3$$

In this case 0.2–0.3 g. of the dry, finely powdered material is placed in the casserole and 3–4 g. of $NaHSO_4$ added. The casserole is then heated, with swirling, over the open flame until the mass is in quiet fusion. (At first the $NaHSO_4$ melts, then decomposes with effervescence into $Na_2S_2O_7 + H_2O$. When this reaction is complete, the mass remains melted and can be heated to a higher temperature without much loss of SO_3.) Heat until SO_3 fumes are recognized, then cover the dish with a watch glass and adjust the flame so as to keep the mixture near this temperature. Continue the reaction for about 15 minutes, then cool, add 20–25 cc. of H_2O, and heat as necessary to dissolve the residue. The anhydrous sulfates may dissolve slowly, sometimes requiring 2–3 hours digesting with hot water. The solution finally obtained may be analyzed in the usual way for metals.

One type of material not included in the discussion thus far, occurs so extensively in minerals and ores that it should be mentioned briefly. This is silicate radical. Highly basic silicates, such as are associated with limestone, may be effectively decomposed with HCl, the silicon precipitating as silicic acid, H_2SiO_3. By careful evaporation on a water bath and drying the residue at 100°–105° for 30 minutes or so, the silicic acid becomes relatively inert. Moisten the residue with 5 cc. of concentrated

HCl, let stand a few minutes to convert any basic salts to normal salts, then add 25–50 cc. of water, stir, filter and wash. The residue will consist of fairly pure silicic acid and may be discarded, the filtrate being examined for the various materials which may be present. In the case of acid silicates, such as clay, direct treatment with HCl is ineffective. In this case the dry material is fused with Na_2CO_3, as described above, which converts the silica to sodium silicate. After cooling, the mass may then be disintegrated by digesting with hot water, the solution then acidified and evaporated as just described to remove the silica.

§315. *Dissolving a Sample for Analysis.* — From various experiments of the types indicated above, using small portions of the original material, the student should be able to decide very definitely the procedure to be employed in dissolving a main portion for analysis. If HCl can be used effectively to dissolve the sample, this is the reagent commonly selected, instead of HNO_3 or HCl + HNO_3, because of the slightly greater ease in the analysis of the resulting solution. If HCl will not dissolve the unknown, but HNO_3 or HCl + HNO_3 will, either of these solvents may be used, that one being preferred which seemed to work best in the preliminary studies. Occasionally, when complete solution cannot be obtained with a single solvent, the material may be dissolved by treating first with HNO_3, and then using HCl on the residue insoluble in HNO_3. Thus with an alloy containing Hg, Ag and Sn: HCl produces no effect; HNO_3 attacks it fairly readily dissolving Hg and Ag, but converting the Sn to the white β-stannic acid; and HCl + HNO_3 dissolve the Hg and Sn, but convert the Ag to AgCl. In such a case it is possible to obtain complete solution by treating first with HNO_3, then filtering out and washing the stannic acid, digesting it for a few minutes at near the boiling point with 5 cc. of concentrated HCl, and finally diluting with water to a volume of about 30 cc. The stannic acid undergoes no visible change on heating with the HCl, but after a few minutes digesting, the precipitate that is left dissolves readily on treating with water. The resulting solution may be used in the ordinary way to test for Sn. Sometimes, as in the case of alloys running high in Al or Cr, the small portion tried originally seemed to dissolve completely in HCl, but when the larger sample is tried, a distinct residue is obtained. This may consist largely of C or H_2SiO_3, but it may also contain small quantities of metals that are insoluble in HCl. Therefore such a residue should be treated carefully with HNO_3 to dissolve such important constituents. Any residue still left may usually be filtered out and discarded, the filtrate being examined for metals not found in the HCl solution.

After the acid treatment has been definitely decided upon (and preparation has been made to apply such tests as should be made during the dissolving process), the normal method of procedure is as follows:

Place about 1 g. of the original, powdered, dry unknown in the casserole,

add 15 cc. of the acid decided upon, heat until the reaction is proceeding readily, apply the tests indicated above, and then continue the reaction until it is completed. Then evaporate the solution down to a volume of about 5 cc. to remove any large excess of acid, dilute with water to 30 cc., place in a tincture bottle, and label the bottle with the name of the acid being used and the identification number of the dry unknown. If the reaction proceeds slowly even at the boiling point, provision should be made to avoid excessive evaporation during the prolonged period of digestion. This may be done by covering the casserole with a watch glass, or, in a more extreme case, the reaction may be carried out in an Erlenmeyer flask with the mouth covered by a small watch glass. In the latter case, the walls of the flask serve to condense the vapors again, while the small opening decreases the amount of diffusion that will take place. The flame should then be so adjusted as to keep the solution barely at the boiling point. Under such conditions the reaction may be continued for half an hour to an hour as necessary, without adding more reagent. Obviously, boiling in an open dish is a very extravagant as well as a discourteous method of carrying out such an operation, though inconvenience to neighbors may be avoided by the use of a hood.

Occasionally it is difficult to judge, by direct observation, whether the reaction is still taking place. If a colored solution is being produced, an increased depth of color may be reassuring evidence; but if the resulting solution is colorless, the slow change in volume of the residue is the only direct way to tell how things are going. In case of doubt, however, the simplest procedure is to pour off the reagent, wash 2–3 times by decantation, then add a fresh portion of the reagent and heat for a little while. Then place a few drops of the resulting solution on a watch glass and evaporate carefully to dryness, comparing the residue left with that obtained by evaporating a corresponding amount of the reagent. In this way it is possible either to avoid wasting excessive time with a reaction that is already complete, or to obtain assurance that a slow reaction may still prove effective.

If more than one solvent is to be used, it is important to carry the reaction of each solvent as far as it will go. Thus in the case of the amalgam mentioned above, the treatment with HNO_3 should be continued until all the Hg and Ag are in solution, the resulting solution finally being filtered, evaporated to about 5 cc., then diluted as usual, and placed in a separate tincture bottle. The residue of β-stannic acid is washed to remove HNO_3 (and $AgNO_3$), then boiled with HCl, and diluted as described above. The two solutions are analyzed separately.

If any of the special procedures are to be resorted to, because of failure to obtain satisfactory results in the preliminary studies with the acids, the details given above may be followed. In such a case use 0.3–0.5 g. of the dry unknown, carry out the treatment as described, and label carefully all

solutions obtained so as to show the procedure followed and the particular solvent used.

§316. *Reporting the Simple Dry Unknowns.* — As a result of physical examination of the material, combined with reactions with various solvents and analysis of the resulting solutions, it should be possible to distinguish definitely the following types of material:

free metal (or non-metal)	normal salt
alloy	acid salt
oxide or hydroxide	basic salt
acid	double salt

In some of these cases additional tests must be tried or supplementary information obtained from the descriptive part of the text to distinguish between certain alternatives. Thus, if one has sifted the evidence to the point of deciding that the material must be either an oxide or a hydroxide, the final distinction between these may be based on (*a*) heating a portion of the dry material in a dry test tube (an oxide is unaffected, while a hydroxide decomposes into oxide and H_2O, the latter condensing on the walls of the test tube). (*b*) The color of the material in cases where the two have different colors (CdO is brown, $Cd(OH)_2$ white; CuO is black, $Cu(OH)_2$ blue; SnO is black, $Sn(OH)_2$ white; etc.). (*c*) By reference to the text it is found that certain hydroxides do not exist in the dry state (Ag, Hg, As, etc.). Again, if one is concerned with the question of whether a particular substance is a normal or basic salt and the material does not dissolve appreciably in water, the descriptive part of the text may indicate that such products, obtained as precipitates, are normal salts in some cases and basic salts in others. In such a case the material should be reported as indicated by the text. Finally, in distinguishing between oxides (or hydroxides) and basic salts, it may be necessary to dissolve a portion of the material in each of two different acids, testing each solution for the acid radical of the other acid. Thus, to distinguish BiOCl or $BiONO_3$ from Bi_2O_3 (or $Bi(OH)_3$), it is necessary to dissolve some of the material in HCl to test for NO_3^-, and to dissolve some more of the material in HNO_3 to test for Cl^-.

In making out a final report of the unknown, the following four points should be covered so far as possible:

(1) a list of metals and acid radicals actually identified,
(2) an approximate statement of whether the constituents listed in (1) are major or minor constituents,
(3) the probable formula of the substance if a simple compound,
(4) the technical name of the material if it is a commercial product (brass, bronze, tin plate, electrical resistance alloy, chrome alum, table salt, etc.).

THE STUDY OF COMPLEX MIXTURES

§317. *An Arbitrary Method of Attack.* — In these cases, as indicated at the beginning of this discussion, there are definite limitations to the effectiveness of chemical examination by the use of the conventional solvents and reagents. Even when water is used, reactions may take place that change the materials considerably from those originally present. Thus, a mixture of Na_2CO_3 and $CaCl_2$ (in equivalent proportions), on treatment with water would be changed into $CaCO_3$ as a precipitate, and NaCl in solution. From analysis of the products, it would be impossible to distinguish between the two limiting cases (a) that the original mixture was composed of Na_2CO_3 and $CaCl_2$, and (b) that the original mixture was composed of $CaCO_3$ and NaCl. Also, it would be possible to mix the first combination with the second in varying proportions and still obtain the same final results after the unknown has been treated with water.

Sometimes it is possible to use inert solvents to test for certain individual constituents of a mixture. Thus carbon bisulfide is an excellent solvent for S°, or I_2, and does not react with other common inorganic substances. Within certain limits, it is possible to separate solids of low specific gravity from those of high specific gravity by the use of certain inert liquids of high density, a practice frequently resorted to in mineralogy. Still other properties may be made the basis of separating other constituents; thus, a magnet might be used to remove Fe°, Fe_3O_4, Ni° and Co° from a mixture. Such schemes have not been worked out with sufficient fullness to make them useful as a systematic procedure for the study of a general mixture. It has seemed best, therefore, not to attempt the use of mechanical means for separating the parts of the mixture and identifying them as individuals.

The scheme that has been employed for a number of years at the University of Michigan, consists in treating the original unknown with water, allowing sufficient time for such dissolving to take place, and for such reactions to occur, as will. This solution, called the water solution, is analyzed in the usual way for metals and for acid radicals, and these are reported in their ionic forms. The residue, insoluble in water, is washed thoroughly, then small quantities of it are subjected to preliminary tests with the usual acid solvents, HCl, HNO_3 and HCl + HNO_3, following the same technique as was indicated in the case of the simpler unknowns just discussed. Following this, the residue is dissolved and analyzed, and the attempt is then made to determine the individual substances present in the residue itself. This last is a simpler case than that of the original dry unknown, since the materials now present are all insoluble in water. It may not be an easy task, however, if the residue contains more than one substance; in fact, it is impossible to distinguish between certain combinations; therefore the problem must be considered solved when a list of

substances has been prepared that will account for all of the data collected concerning a particular residue.

§318. *The preparation of the water solution* is carried out as follows: Place about 1.5 g. of the well-powdered, dry unknown in the casserole, add 50 cc. of water, cover with a watch glass, then heat to boiling. Apply tests for gases evolved and, if the material does not dissolve completely, let it digest at near the boiling point for about 10 minutes. Cool, filter, and place the filtrate in a tincture bottle, labelling it properly with the name of the solvent and the identifying mark of the dry unknown.

During the preparation of the water solution, a great variety of reactions may occur, some involving the production of gases which escape from the solution. Thus, substances which dissolve in (or react with) water to form an acid solution, will react with alkali carbonates and sulfides to liberate CO_2 and H_2S. In extreme cases, such reactions may take place with some of the insoluble carbonates and sulfides. For example, $AlCl_3$ will react with $BaCO_3$, to form $Al(OH)_3$, $BaCl_2$, CO_2 and H_2O; and $NaHSO_4$ will react with FeS to form Na_2SO_4, $FeSO_4$ and H_2S. If excess of $AlCl_3$ or $NaHSO_4$ is present, the process may involve the complete loss of carbonate and sulfide radicals from the solution. In the case of substances which dissolve in (or react with) water to form an alkaline solution, the presence of ammonium salts may be overlooked, due to their conversion to NH_4OH and loss of NH_3 in the preparation of the water solution. $Na_2CO_3 + 2\ NH_4Cl = 2\ NaCl + 2\ NH_3 + CO_2$; $Ba(OH)_2 + 2\ NH_4Cl = BaCl_2 + 2\ NH_3 + 2\ H_2O$.

§319. *In studying the residue from the water solution*, the first step is similar to that taken with the simple dry unknowns, namely, trying the action of HCl, HNO_3 and HCl + HNO_3, separately, on small portions of the material. The results may not be so definite, however, due to the possible presence of two materials which differ in their reactions with the acids. Not infrequently a mixture which is insoluble in any one acid solvent may be dissolved without resorting to special methods if the different acids are used in the proper order. Of the materials which can be dissolved in the common acids, Sb and Sn as metals or compounds, Al and Cr as metals (or alloys running high in these metals), higher oxides of Pb, Mn, Co and Ni, and HgS, are insoluble in HNO_3 under ordinary treatment; while Ag and large amounts of Pb as metals or compounds, are insoluble (or not completely soluble) in either HCl or HCl + HNO_3. With mixtures containing representatives of these two groups of substances, it is possible to get complete solution by using HNO_3 first, to dissolve the Ag and Pb, then treating the residue with HCl, and dissolving the remaining constituents in HCl + HNO_3. The order suggested, using HNO_3 first, avoids the formation of AgCl and $PbCl_2$ if either of these metals is present.

On the other hand, the difficulties encountered when Sn and its compounds are treated with HNO_3, including both the filtering and the dissolving of the β-stannic acid, may be sufficient to make it simpler in such a case to treat with HCl first and handle Ag and Pb by special procedures. In such a case, it might still be worth while to treat part of the material with HNO_3, so as to distinguish between chlorides of Ag and Pb present in the residue from the water solution and those formed from treatment with HCl (or HNO_3 + HCl). From the appearance of the reactions in the preliminary tests, it is sometimes possible to judge which type of situation one is dealing with. In other cases, it may be desirable to try both procedures on a small scale so as to select the better one when ready to dissolve the main portion of the residue. Sometimes the use of a reductant (CH_2O) along with HNO_3 may make it possible to dissolve the residue completely in HNO_3, when otherwise two acid solutions might be required (this covers the case of higher oxides).

It will be noted that the use of the special procedures directly on the residue from the water solution has not been recommended. These have been omitted purposely thus far, because it will be an exceptional case which contains nothing to dissolve in the acids. It is expected, therefore, that the residue will be subjected to systematic treatment with the acids, so that as much as possible will be dissolved in this way. Only after this has been done should the special methods for treatment of substances insoluble in the acids be tried.

After the preliminary studies on the behavior of the acids have been completed, a definite plan should be formulated for treatment of the residue with the acid solvents. The general procedure for treating with a given acid is the same as described under the discussion of simple dry unknowns. If the treatment involves the use of successive acids, the reaction should be continued in each case until definite evidence is obtained that it has gone as far as it will. The solution is then filtered, the residue washed, and treatment with the next acid undertaken.

When treating the residue from the water solution with acids, various reactions may occur that will need to be recognized. These were considered in the earlier discussion and need not be repeated in detail at this time. It must be noted, however, that more than one of these reactions may occur, so the situation is more complex than in the earlier case. Thus, a mixture of Fe° and $CdCO_3$ in dissolving in HCl, would give off both H_2 and CO_2; and a mixture of Ag_2CO_3 and Ag_2S would give off CO_2 and brown fumes with HNO_3. On the other hand, a mixture of $Fe(OH)_3$ and ZnS might dissolve in HCl without evolution of H_2S, the sulfide radical being oxidized to S° by the Fe^{+3}. Similarly, a mixture of Fe° and MnO_2 might dissolve in HCl without evolution of Cl_2, due to reduction of the MnO_2 by the Fe° or Fe^{++} in the presence of the acid. After treatment with HNO_3, the test for Cl_2 evolved when treating the residue with HCl may be due to NO_3^-

not completely washed out of the residue, rather than to an oxidant that was present in the residue before HNO_3 was used. Finally, the test for H_2 (by odor) fails when a sulfide is present, due to the H_2S evolved. It will be seen, therefore, that it may be necessary to depend on such items as color, and differences in behavior with the different acids, in order to identify certain materials in combination, while in other cases it will be impossible to distinguish definitely between certain possibilities. For this reason, it is necessary to emphasize again that the problem must be considered solved when a list of chemical substances has been submitted that will account for the facts that should be available as a result of the studies suggested.

After the treatment with acids, a residue may be left which will require the use of special reagents to be dissolved or to be converted into materials which can be dissolved readily. If there is a moderate amount of such residue, it may be worth while to try exploratory tests on separate portions of it, following the suggestions made in the previous discussion. If the quantity of residue is small, it may be best to use all of it, trying one procedure after another (the order being based on guesses as to what it may be, as judged from color and other physical characteristics) until an effective treatment is found. Of the different procedures suggested, the fusion with alkali carbonate is usually reserved as a last resort. A proper combination of treatment with Zn and dilute sulfuric acid (for insoluble halides), boiling with concentrated Na_2CO_3 solution (for insoluble sulfates), and fusing in a casserole with $Na_2S_2O_7$, will take care of the great majority of cases.

§320. *Reporting the Complex Dry Unknown.* — After the solutions have been prepared and analyzed and the various bits of data all collected, the next problem is to make out a report for the dry unknown. In accordance with the arbitrary system of study suggested above, the report should not attempt to indicate the substances present in the original mixture, nor should it merely list the metals and acid radicals identified. The final report should cover the following four items;

(a) gases identified while preparing the water solution,
(b) ions found in the water solution,
(c) outlines of procedure used to dissolve the residue,
(d) substances judged to be present in the residue.

INTERFERENCE OF METALS WITH THE TESTS FOR ACID RADICALS

§321. It was stated at the beginning of the discussion on acid radicals that the procedures described assumed that no metals would be present which would interfere with the direct application of the methods given

It is entirely possible, however, to have a solution to analyze which may contain various combinations of both metals and acid radicals. This is a situation which will arise commonly in the analysis of dry unknowns, particularly with the complex mixtures. The chief irregularities thus introduced into the systematic testing for the metals were discussed on p. 363–9. To that discussion might be added the fact that with strong oxidants in the solution, when H_2S is passed in for the precipitation of Group II, especially As^{V}, oxidation of part of the H_2S to S° will take place, with some resulting confusion. Again, with high concentration of I^- present, oxidation of Fe^{++} at the beginning of Group III presents some trouble. In this case, the I^- is oxidized to I_2 which should be removed by volatilization before testing for completeness of oxidation of Fe^{++}.

The reverse case, involving interferences with the ordinary schemes of testing for acid radicals, is taken care of in part by the procedures used to dissolve the dry unknown. The preparation of a water solution may separate certain water-soluble constituents from others which are insoluble in water, thus avoiding complications that might arise if the dry unknown were treated directly with acids. In a similar way, the further separation of the residue into acid-soluble and acid-insoluble constituents may simplify the analysis of the resulting solutions. The chief difficulty to be encountered is the presence of metals and of acid radicals in the acid solution such that on neutralization, corresponding salts may precipitate. It will be recalled, however, that few of the confirmatory tests for the acid radicals are carried out in neutral solution. In cases where preliminary separations require precipitation under such conditions, the formation of precipitates by neutralization of the solution will not interfere generally with the confirmatory tests to be used, providing care is taken to ensure adequate treatment of the neutral solution and precipitate with the additional precipitating agent. If it is desired to separate the heavy metals from the acid radicals before testing for the latter, this can be done fairly effectively by adding to the solution 10–15 cc. excess of 3 *N* Na_2CO_3 and boiling a short time. This precipitates the heavy metals generally as carbonates (Fe^{+3}, etc., as hydroxides), which may be filtered out and discarded. A small portion of the filtrate is acidified with HNO_3 and the test for Cl^- applied; the remainder is acidified with HCl and the tests for the other acid radicals applied.

Another difficulty may be encountered when metals are present that give precipitates with Cl^- or SO_4^{--}, and these radicals are added in the tests for certain of the acid radicals. In testing for SO_4^{--} with $BaCl_2$ and HCl, the metals of Group I would cause trouble. In this case, the metals might be removed with HCl, or $Ba(NO_3)_2$ and HNO_3 might be used instead of $BaCl_2$ and HCl. In the $CaSO_4$ test for an oxalate, the presence of metals forming insoluble sulfates would make the test ineffective. In this case, a correspondingly dilute solution of $CaCl_2$ or $Ca(NO_3)_2$ might be used.

In using $K_2S_2O_8$ to test for (or remove) I^- or Br^-, and in using $FeSO_4$ and H_2SO_4 in the brown-ring test for a nitrate, insoluble sulfates may precipitate. The sodium carbonate method recommended above will avoid this; or the metals may be precipitated with slight excess of dilute H_2SO_4 and filtered out before these other tests are applied.

If one were analyzing complex solutions, the situation might be more difficult than in the case of dry unknowns. Excess of NaOH or NH_4OH might be present, such that complex ammonia ions or anions of the amphoteric acids could be associated with acid radicals that would be incompatible with the corresponding simple positive ions. If such a solution were neutralized, various precipitates would form which might cause distinct trouble in identifying either the metal or the acid radical. For example, a solution containing PbO_2^{--} along with SO_4^{--}, or $Ag(NH_3)_2^+$ along with Cl^- and Br^-, would provide obvious complications. In such a case, it might be desirable or necessary to filter out the precipitate obtained on neutralization and treat it as a dry unknown in testing for both metal and acid radical. Other complications of this type are mentioned on p. 187, note 2, which should be consulted in this connection.

§322. REACTIONS OF A FEW COMMON REAGENTS

1. Soluble chlorides, nitrates and sulfates of many of the heavy metals give precipitates by hydrolysis, therefore they require more or less of the corresponding free acids to form stable aqueous solutions. This situation is most marked with Bi, Sb, Sn and Hg (except $HgCl_2$); less so with Pb, Fe, Cr and Al; and slight with Cu, Co, Ni, Mn, Cd and Zn.

2. Most reagents are capable of entering into several different kinds of reaction, such as double decomposition, displacement, oxidation, reduction, formation of complex compounds, etc. For example: Hydrochloric acid (a) as a strong acid, will neutralize bases and interact with metallic oxides and hydroxides with formation of salts and water; (b) as a mild oxidant, will oxidize metals above hydrogen in the electromotive series to positive ions (the hydrogen ion being reduced to H_2); (c) as a mild reductant, will reduce various strong oxidants such as HNO_3, $K_2Cr_2O_7$, Pb_3O_4, $KMnO_4$, etc. (the chloride ion being oxidized to Cl_2); (d) as a soluble, highly ionized chloride, will form insoluble chlorides with silver, lead and mercurous ions; (e) as a soluble, highly ionized chloride, will combine at higher concentrations, with AgCl, $PbCl_2$, etc., forming complex ions, $AgCl_3^{--}$, $PbCl_4^{--}$, etc., which increases the solubility of such precipitates very appreciably.

3. HI (or KI in acid solution) shows behavior similar to HCl, except that HI is a stronger reductant than HCl, being oxidized to I_2 by such mild oxidants as $FeCl_3$, $CuCl_2$, etc., and enters more readily into the formation of complexes. Of the latter, BiI_4^- is important as a means of identifying

Bi, and HgI_4^{--} is important as the base of Nessler's reagent, used in testing for NH_3. Further, by formation of the latter complex ion, HI will dissolve Hg with evolution of H_2, contrary to expectation from the electromotive series. The insoluble iodides are AgI, PbI_2, Hg_2I_2, HgI_2, BiI_3, Cu_2I_2.

4. NaOH (and other strong alkalis such as KOH and $Ba(OH)_2$) (a) will neutralize acids; (b) will oxidize Al, Zn and, less readily, Cr, to AlO_2^-, ZnO_2^{--} and CrO_2^- with evolution of H_2; (c) will precipitate oxides of Ag^+, Hg_2^{++}, Hg^{++} and Sb^{+3}, and hydroxides of the other common metals except the alkalis and alkaline earths. The following insoluble hydroxides are amphoteric: $Pb(OH)_2$, $Al(OH)_3$, $Cr(OH)_3$, $Zn(OH)_2$, $Sn(OH)_2$, $SnO(OH)_2$, $Sb(OH)_3$, $SbO(OH)_3$. They dissolve in excess of strong alkali by neutralization, forming: PbO_2^{--}, AlO_2^-, CrO_2^-, ZnO_2^{--}, SnO_2^{--}, SnO_3^{--}, SbO_2^-, SbO_4^{-3}. The failure of As to precipitate with NaOH is due to the solubility of the hydroxides (acids) in water.

5. NH_4OH, (a) as a weak base, will neutralize the common acids, though the very weak acids — including the amphoteric hydroxides listed in (4) — are not acted upon to more than a slight extent; (b) as a mild reductant, will reduce (especially in the presence of NaOH, etc.) some of the stronger oxidants, such as Cl_2, Br_2 and $KMnO_4$, to Cl^-, Br^- and MnO_2, the NH_4OH being oxidized to N_2; (c) as a precipitating agent, will precipitate the oxides of Ag and Sb, and hydroxides of the other common metals except the alkalis, alkaline earths and mercury. In the latter case, mercuric amino compounds are precipitated, e.g., Hg_2Cl_2 forms $HgNH_2Cl + Hg$; $HgCl_2$ forms $HgNH_2Cl$; (d) as an unstable compound, supplies NH_3 which will combine with Ag^+, Cu^{++}, Cd^{++}, Co^{++}, Ni^{++} and Zn^{++} to form complex ions (for which we adopt the simple formula with two molecules of ammonia associated with each valence of the metallic ion). This reaction takes place readily enough to dissolve the common precipitates of these metals, such as the oxides, hydroxides, carbonates, phosphates, etc., in fact, all but the most insoluble compounds such as the sulfides, AgI, and $Ni(C_4H_7N_2O_2)_2$.

6. H_2S, (a) as a weak acid, is neutralized by high concentrations of strong bases such as NaOH and $Ba(OH)_2$, but incompletely by NH_4OH; (b) as a fairly strong reductant, will reduce HNO_3, $K_2Cr_2O_7$, $KMnO_4$, $FeCl_3$, etc., being oxidized to S° or even to H_2SO_4 by the stronger oxidizers; (c) as a precipitating agent, will precipitate sulfides of Ag, Hg (Hg_2^{++} forms HgS + Hg), Bi, Cu, As, Sb, Sn, Pb, Cd, Zn, Fe, Co, Ni and Mn. Of these, the sulfides of Ag, Hg, Bi and Cu form readily in alkaline, neutral, or even strongly acid solution; those of Pb, Cd and Zn precipitate readily in alkaline, neutral or very slightly acid solution; those of Fe, Co, Ni and Mn precipitate readily only in alkaline solution. The sulfides of As, Sn^{+4} and Sb^{+5} precipitate only in acid solution. In alkaline solution H_2S will dissolve As_2S_3, As_2S_5, SnS_2 and Sb_2S_5, forming thio ions, e.g., AsS_4^{-3}, SnS_3^{--} and SbS_4^{-3}.

7. NaCN, as a salt of a very weak acid, will neutralize acid solutions, setting free HCN, which is extremely poisonous. (*Precaution! Do not add NaCN to an acid solution.*) As a reductant, it will reduce copper to the cuprous condition, permanganate and manganate to manganese dioxide, the cyanide being oxidized to cyanogen or a cyanate [$(CN)_2$ [1] or NaCNO]. As a precipitating agent, NaCN will precipitate all the common metals except the alkalis, alkaline earths and mercury. With ferric iron, chromium and aluminum, the precipitate is an hydroxide; in the other cases, a cyanide. The less soluble cyanides are Ag, Pb, Bi, Cu, Cd, Co, Ni, Zn, Mn. Many of the metals form double or complex cyanides with excess of the reagent. Formulas for the more common of these are as follows: $NaAg(CN)_2$, $Na_3Cu(CN)_4$, $Na_2Cd(CN)_4$, $K_4Fe(CN)_6$, $K_3Fe(CN)_6$, $Na_4Co(CN)_6$, $Na_3Co(CN)_6$, $Na_2Ni(CN)_4$ and $Na_2Zn(CN)_4$. Potassium ferro- and ferri-cyanides are important reagents, both in analytical chemistry and elsewhere.

8. Na_2CO_3 (or K_2CO_3) (a) will neutralize the common acids, with evolution of CO_2 (with the very weak acids, including the amphoteric hydroxides — see 4 — this takes place to only a very slight extent); (b) will dissolve Al and Zn slowly with formation of AlO_2^- and ZnO_2^{--} and evolution of CO_2 and H_2; (c) as a precipitating agent, will precipitate Sb_2O_3, and hydroxides of Sn^{+4}, Fe^{+3}, Cr^{+3} and Al^{+3}, and normal or basic carbonates of the rest of the common metals except $HgCl_2$ (which forms an oxychloride), the alkalis, and NH_4^+. The carbonates of Ag, Cu and Hg form oxides on heating.

9. The order in which the metals displace each other from combination is conveniently shown by the electromotive series, with the most electropositive metals first as follows: K, Na, Ba, Sr, Ca, Mg, Al, Mn, Zn, Fe, Cd, Co, Ni, Sn, Pb, H, Sb, Bi, As, Cu, Hg, Ag, Pt, Au.

§322a. SOLUBILITIES IN A FEW COMMON SOLVENTS

Four solvents most frequently used in analytical chemistry are water, hydrochloric acid, nitric acid and nitrohydrochloric acid (aqua regia). A knowledge of their behavior with the metals and their common compounds is very useful in qualitative analysis as well as important general information. The following discussion summarizes this material.

The substances considered are free metals, metallic oxides, hydroxides and salts. The salts covered are the nitrates, chlorates, acetates, chlorides, iodides, sulfides, sulfates, carbonates, oxalates and phosphates. The oxides included are the ordinary salt-forming oxides and the more common of the higher oxides. (By salt-forming oxide is meant one that can be converted to a salt without oxidation or reduction, e.g., PbO, which dis-

[1] To avoid the evolution of poisonous $(CN)_2$, the solution should always be alkaline. $(CN)_2 + 2\ NaOH = NaCN + NaCNO + H_2O$.

solves in nitric acid to form a salt, $Pb(NO_3)_2$. By higher oxide is meant one which needs to be reduced in forming a salt, e.g., PbO_2, which does not dissolve in nitric acid directly, but can be dissolved if a reductant, such as sodium nitrite, formaldehyde, or hydrogen peroxide, is used along with the nitric acid.) The metals included are those studied in the usual course, silver, lead, mercury, bismuth, copper, cadmium, arsenic, antimony, tin, iron, chromium, aluminum, cobalt, nickel, manganese, zinc, barium, strontium, calcium, magnesium, sodium, potassium (and ammonium radical). (Note: Arsenic is classed here as a metal, yet the only common salts in which arsenic is the positive radical are the sulfides. The usual salts of arsenic are the arsenites and arsenates, which are similar to phosphates in solubilities.)

I. Water as Solvent.

(a) *Metals.*

None of the metals are appreciably soluble as such in water. A few of the more electropositive ones displace hydrogen, forming the positive ion of the metal. There is corresponding accumulation of hydroxyl ion in the solution, so the metal may then precipitate as the hydroxide if the latter is relatively insoluble. The alkali metals (Na, K, NH_4) dissolve readily in water by this reaction; the alkaline earth metals (Ba, Sr, Ca) are moderately to slightly soluble in water; and Mg, Zn and Al react slowly with water with evolution of hydrogen and precipitation of the hydroxides.

(b) *Oxides and hydroxides.*

The oxides and hydroxides of the alkali metals dissolve readily in water, those of the alkaline earth metals are slightly soluble in water, and the acid-forming oxides and hydroxides of certain of the metals dissolve more or less readily. This last group includes As_2O_3, As_2O_5, CrO_3 and Mn_2O_7, which dissolve in water to form the acids H_3AsO_3, H_3AsO_4, H_2CrO_4 and $HMnO_4$, respectively.

(c) *Salts.*

Many of the salts listed as soluble in water undergo sufficient hydrolysis to form precipitates of hydroxides or basic salts of the metals. In such cases it is necessary to use more or less of the corresponding free acid to overcome this. The effect is most marked with the salts of Hg (both valences except $HgCl_2$), Bi, Sb, Sn; less so with Pb (none in the case of $Pb(C_2H_3O_2)_2$), Fe, Cr, Al; and slight with Cu, Co, Ni, Mn, Cd and Zn.

Acetates, nitrates and *chlorates* of the metals are readily soluble in water.

Chlorides are generally soluble; AgCl, Hg_2Cl_2, BiOCl and SbOCl are insoluble; $PbCl_2$ is slightly soluble.

Iodides are generally soluble; AgI, PbI_2, Hg_2I_2, HgI_2, Cu_2I_2, BiOI and SbOI are insoluble; BiI_3 and SnI_2, slightly soluble.

Sulfides are generally insoluble, Ba, Sr and Ca sulfides being slightly soluble; Na, K and NH_4 sulfides, readily soluble. The sulfides of Al, Cr and Mg can only be prepared in the dry way; on treating them with water, they are hydrolyzed completely into the hydroxides and hydrogen sulfide.

Sulfates are generally soluble; $PbSO_4$, Hg_2SO_4, $BaSO_4$ and $SrSO_4$, insoluble; Ag_2SO_4, $HgSO_4$ and $CaSO_4$ slightly soluble.

Carbonates are generally insoluble, the metals whose carbonates are soluble being Na, K and NH_4. The following metals do not form carbonates: As, Sn, Sb, Fe^{III}, Cr and Al. This is due to the fact that any reagent which supplies carbonate ion will also supply an appreciable concentration of hydroxyl ion (by hydrolysis), and the hydroxides of these metals are less soluble than the carbonates.

Oxalates are generally insoluble, the metals whose oxalates are soluble being Sn^{IV}, Na, K and NH_4.

Phosphates are generally insoluble; the metals whose phosphates are soluble being Na, K and NH_4.

II. Hydrochloric Acid as Solvent.

Chemical reactions are involved in using hydrochloric acid to dissolve any of the substances that are insoluble in water. In the following statements, only those cases will be discussed in which the substance is insoluble or slightly soluble in water.

(a) *Metals.*

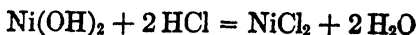
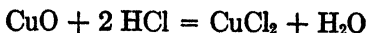
The reaction involved in dissolving a metal in hydrochloric acid is the oxidation of the metal to a metallic ion by the hydrogen ion, the latter being reduced to hydrogen. The ordinary molecular equation is written as follows: $Zn + 2\,HCl = ZnCl_2 + H_2$. In the cases of Sn and Fe, the oxidation is carried only to the lower valence, $SnCl_2$ and $FeCl_2$.

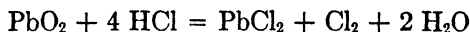
Hydrochloric acid will not dissolve the metals below hydrogen in the electromotive series (i.e., Ag, Hg, Bi, Cu, As, Sb); it dissolves slowly Pb, Co, Ni, Cr and Cd; it dissolves readily Sn, Zn, Al, Fe, Mn and Mg.

(b) *Oxides and hydroxides.*

The reaction involved in dissolving a salt-forming oxide or hydroxide in hydrochloric acid is neutralization. The molecular equations are written as follows:

$$CuO + 2\,HCl = CuCl_2 + H_2O$$

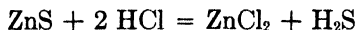
$$Ni(OH)_2 + 2\,HCl = NiCl_2 + 2\,H_2O$$

In the case of higher oxides the hydrochloric acid may also function as a mild reductant, reducing the metal to a lower valence, itself being oxidized in part to chlorine.

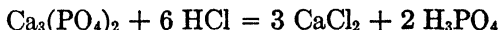
$$PbO_2 + 4\ HCl = PbCl_2 + Cl_2 + 2\ H_2O$$

Hydrochloric acid will dissolve all the common oxides and hydroxides of the metals (including the higher oxides), except

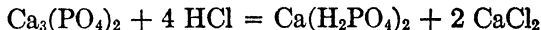
(1) metals of Group I, which are converted to insoluble or slightly soluble chlorides;
(2) certain oxides which have been ignited (i.e., heated to a high temperature for some time), including SnO_2, Al_2O_3, Cr_2O_3 and Fe_2O_3.

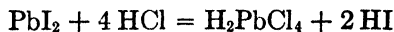
(c) *Salts.*

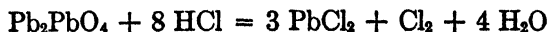
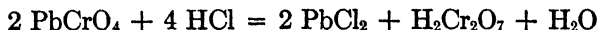
The reaction involved in dissolving a salt in hydrochloric acid is, typically, the combining of hydrogen ion from the hydrochloric acid with the anion of the salt to form a slightly dissociated acid.

$$ZnS + 2\ HCl = ZnCl_2 + H_2S$$

In the case of salts whose anions have valences higher than one, it is frequently possible to dissolve the salt by using so small an amount of hydrochloric acid that the reaction is to be considered as forming an acid salt rather than the free acid. Thus: the ordinary equation for the dissolving of calcium phosphate in hydrochloric acid is written:

$$Ca_3(PO_4)_2 + 6\ HCl = 3\ CaCl_2 + 2\ H_3PO_4$$

but it is possible to dissolve the salt under such conditions that the equation should be written:

$$Ca_3(PO_4)_2 + 4\ HCl = Ca(H_2PO_4)_2 + 2\ CaCl_2$$

In a few cases the hydrochloric acid may act as solvent by supplying a high concentration of chloride ion which reacts with the cation of the salt to form a complex ion. This is the reaction in the dissolving of silver chloride, or lead iodide, in hydrochloric acid.

$$AgCl + 2\ HCl = H_2AgCl_3$$
$$PbI_2 + 4\ HCl = H_2PbCl_4 + 2\ HI$$

Certain salts whose anions are strong oxidants may be partly or wholly reduced in the process of dissolving in hydrochloric acid.

$$2\ PbCrO_4 + 4\ HCl = 2\ PbCl_2 + H_2Cr_2O_7 + H_2O$$
$$2\ PbCrO_4 + 16\ HCl = 2\ PbCl_2 + 2\ CrCl_3 + 8\ H_2O + 3\ Cl_2$$
$$Pb_2PbO_4 + 8\ HCl = 3\ PbCl_2 + Cl_2 + 4\ H_2O$$

Chlorides, insoluble in water, do not dissolve readily in hydrochloric acid, except BiOCl, SbOCl and Cu_2Cl_2. AgCl and $PbCl_2$ are slightly soluble in concentrated hydrochloric acid.

Iodides, insoluble in water, do not dissolve readily in hydrochloric acid, except BiOI and SbOI. PbI_2 is slightly soluble in concentrated hydrochloric acid.

Sulfides, insoluble in water, which dissolve readily in hydrochloric acid are PbS, CdS, SnS, SnS_2, FeS, MnS and ZnS; sulfides which dissolve with difficulty are Bi_2S_3, CuS, Sb_2S_3, Sb_2S_5, CoS and NiS; sulfides insoluble in hydrochloric acid are Ag_2S (forms AgCl + H_2S), HgS, As_2S_3 and As_2S_5.

Sulfates, insoluble in water, are only slightly soluble in hydrochloric acid.

Carbonates, insoluble in water, are soluble in hydrochloric acid, except that Group I metals are converted to chlorides in the process.

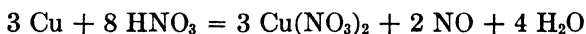
Oxalates, insoluble in water, are soluble in hydrochloric acid, except that Group I metals are converted to chlorides in the process.

Phosphates, insoluble in water, are soluble in hydrochloric acid, except that Group I metals are converted to chlorides in the process. Stannic phosphate dissolves with difficulty in hydrochloric acid.

III. Nitric Acid as Solvent.

(a) *Metals.*

The reaction involved in dissolving a metal in nitric acid is oxidation of the metal to a metallic ion and reduction of the nitric acid to nitric oxide. The ordinary molecular equation is written as follows:

$$3\ Cu + 8\ HNO_3 = 3\ Cu(NO_3)_2 + 2\ NO + 4\ H_2O$$

With fairly concentrated nitric acid and metals toward the lower end of the electromotive series, the reduction product of the nitric acid will be nitrogen dioxide or nitrous acid; while with rather dilute nitric acid and metals toward the upper end of the electromotive series, the nitric acid will be reduced to nitrous oxide and even hydrazine or ammonium nitrate.

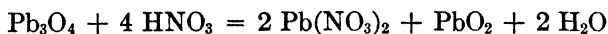
Nitric acid will dissolve all the metals except Al, Cr, Sn and Sb. Al and Cr become passive on treatment with nitric acid; Sn and Sb are acted upon readily, but form white precipitates of β-stannic acid, $(H_2SnO_3)_x$, and antimonic acid, H_3SbO_4. In reacting with Sn and Fe, the nitric acid oxidizes these metals to their higher valences (Sn = 4, Fe = 3). Mercury may be dissolved as mercurous nitrate, but heating with excess of nitric acid oxidizes this to mercuric nitrate. Arsenic, on dissolving in nitric acid, forms arsenic acid, H_3AsO_4, instead of a nitrate.

$$3\ As + 5\ HNO_3 + 2\ H_2O = 3\ H_3AsO_4 + 5\ NO$$

Nitric acid is much more effective as a solvent for the metals than hydrochloric acid, except for the three metals Sn, Al and Cr.

(b) *Oxides and hydroxides.*

The reaction involved in dissolving a salt-forming oxide or hydroxide in nitric acid is primarily neutralization. Compounds of Hg, Sb, Sn, As and Fe exhibiting lower valences of these metals are oxidized to compounds with higher valences (Hg = 2, Sb = 5, Sn = 4, As = 5, Fe = 3) by boiling with nitric acid. In the case of higher oxides, nitric acid is ineffective as a solvent, though it will react with mixed oxides (oxides having both salt-forming and non-salt-forming valences of metal present) to form the nitrate and higher oxide of the metal.

$$Pb_3O_4 + 4\ HNO_3 = 2\ Pb(NO_3)_2 + PbO_2 + 2\ H_2O$$

Nitric acid will dissolve all the common oxides and hydroxides of the metals except

(1) higher oxides of Pb, Mn, Co and Ni,
(2) Sn and Sb (converted to $(H_2SnO_3)_x$ and H_3SbO_4),
(3) SnO_2, Al_2O_3 Cr_2O_3 and Fe_2O_3.

(c) *Salts.*

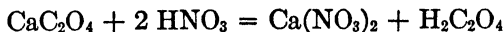
The reaction involved in dissolving a salt in nitric acid is, typically, the combining of hydrogen ion from the nitric acid with the anion of the salt to form a slightly dissociated acid. In the case of salts whose anions are easily oxidized (sulfides, sulfites and iodides), the removal of anion is commonly caused by oxidation (to free sulfur, sulfate ion, or free iodine), rather than by forming a slightly dissociated acid. Compounds of Hg, As, Sb, Sn and Fe exhibiting lower valences of these metals are oxidized to higher valences (Hg = 2, As = 5, Sb = 5, Sn = 4, Fe = 3).

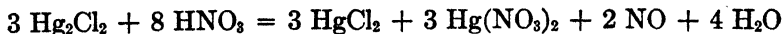
Equations:

$$CaC_2O_4 + 2\ HNO_3 = Ca(NO_3)_2 + H_2C_2O_4$$

$$3\ CuS + 8\ HNO_3 = 3\ Cu(NO_3)_2 + 2\ NO + 3\ S + 4\ H_2O$$

$$3\ PbI_2 + 8\ HNO_3 = 3\ Pb(NO_3)_2 + 3\ I_2 + 2\ NO + 4\ H_2O$$

$$FeS + 4\ HNO_3 = Fe(NO_3)_3 + S + NO + 2\ H_2O$$

Chlorides, insoluble in water, do not dissolve readily in nitric acid, except BiOCl and Cu_2Cl_2. $PbCl_2$ is slightly soluble in nitric acid, being oxidized to free chlorine by digesting with the hot acid. Hg_2Cl_2 reacts slowly with nitric acid to form $HgCl_2$ and $Hg(NO_3)_2$.

$$3\ Hg_2Cl_2 + 8\ HNO_3 = 3\ HgCl_2 + 3\ Hg(NO_3)_2 + 2\ NO + 4\ H_2O$$

Iodides, insoluble in water, dissolve in nitric acid as follows: AgI insoluble; Hg_2I_2, HgI_2 and Cu_2I_2 dissolve slowly; PbI_2, BiOI and BiI_3 dissolve fairly readily on boiling with excess of nitric acid; SbOI and SnI_2

are readily oxidized to iodine, but the Sb and Sn form H_3SbO_4 and $(H_2SnO_3)_x$, respectively.

Sulfides, insoluble in water, dissolve generally in nitric acid, except HgS, which reacts only slowly with fairly concentrated nitric acid; and sulfides of Sn and Sb, which react readily but are converted to white precipitates of antimonic and β-stannic acids.

Sulfates, insoluble in water, are only slightly soluble in nitric acid; though mercurous sulfate dissolves slowly on boiling, due to oxidation to mercuric sulfate.

Carbonates, insoluble in water, are soluble in nitric acid.

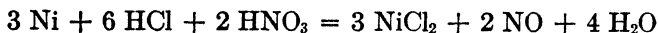
Oxalates, insoluble in water, are soluble in nitric acid.

Phosphates, insoluble in water, are soluble in nitric acid, except stannic phosphate, which is inert toward nitric acid.

IV. Nitrohydrochloric Acid (Aqua Regia) as Solvent.

(a) *Metals.*

The reaction involved in dissolving a metal in nitrohydrochloric acid is, typically, the oxidation of the metal to a metallic ion and the reduction of the nitric acid to nitric oxide. Since the two reagents are commonly mixed in such proportions that the nitric acid may all be reduced to nitric oxide, the ordinary molecular equation assumes the chloride of the metal to be formed.

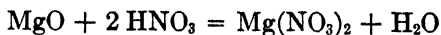
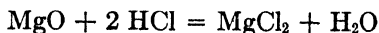
$$3\ Ni + 6\ HCl + 2\ HNO_3 = 3\ NiCl_2 + 2\ NO + 4\ H_2O$$

In the case of arsenic, the compound formed is arsenic acid, rather than a chloride of arsenic, since the latter, when made by direct action of chlorine on arsenic, is fully hydrolyzed by water into arsenic acid and hydrochloric acid.

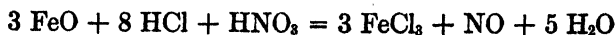
Nitrohydrochloric acid will dissolve all the metals except Ag, the latter being converted to AgCl. The higher valences are obtained in the case of Hg, As, Sb, Sn and Fe (i.e., Hg = 2, As = 5, Sb = 5, Sn = 4, Fe = 3).

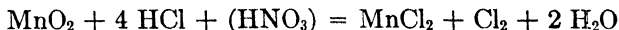
(b) *Oxides and Hydroxides.*

The typical reaction in dissolving oxides and hydroxides in nitrohydrochloric acid is neutralization. In such a case, write two separate equations showing the action of hydrochloric acid and nitric acid individually.

$$MgO + 2\ HCl = MgCl_2 + H_2O$$

$$MgO + 2\ HNO_3 = Mg(NO_3)_2 + H_2O$$

If the metal may be oxidized to a higher valence by the nitrohydrochloric acid, the equation is commonly written showing the nitric acid reduced to nitric oxide and the chloride of the metal formed.

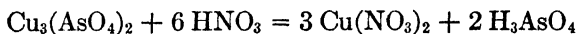
$$3\ FeO + 8\ HCl + HNO_3 = 3\ FeCl_3 + NO + 5\ H_2O$$

Higher oxides dissolve less readily in nitrohydrochloric acid than in hydrochloric acid alone. The reaction is the same in both cases, only in the former the hydrochloric acid is diluted by the nitric acid. By enclosing the nitric acid in parenthesis it is shown that nitric acid is present but not used as a reagent in the equation.

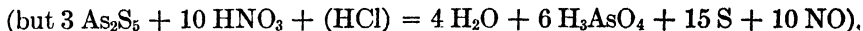
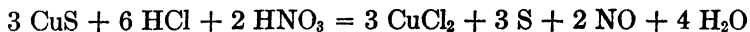
$$MnO_2 + 4\ HCl + (HNO_3) = MnCl_2 + Cl_2 + 2\ H_2O$$

Nitrohydrochloric acid dissolves the common oxides and hydroxides of the metals, except:

(1) Ag (forms AgCl),
(2) the higher oxides of Pb, Co, Ni and Mn, which dissolve better in HCl alone,
(3) ignited oxides SnO_2, Al_2O_3, Cr_2O_3 and Fe_2O_3.

(c) *Salts.*

The typical reaction in dissolving salts in nitrohydrochloric acid is the combining of hydrogen ion from the acids with the anion of the salt to form a slightly dissociated acid. In such a case write two separate equations, showing the action of hydrochloric acid and of nitric acid individually.

$$Cu_3(AsO_4)_2 + 6\ HCl = 3\ CuCl_2 + 2\ H_3AsO_4$$
$$Cu_3(AsO_4)_2 + 6\ HNO_3 = 3\ Cu(NO_3)_2 + 2\ H_3AsO_4$$

If either the cation or the anion (or both) of the salt is oxidized by the nitrohydrochloric acid, then the nitric acid is considered to be used up in this way, the chloride of the metal usually being formed.

$$3\ CuS + 6\ HCl + 2\ HNO_3 = 3\ CuCl_2 + 3\ S + 2\ NO + 4\ H_2O$$
$$(\text{but } 3\ As_2S_5 + 10\ HNO_3 + (HCl) = 4\ H_2O + 6\ H_3AsO_4 + 15\ S + 10\ NO).$$

Chlorides, insoluble in water, are generally soluble in nitrohydrochloric acid, except AgCl. Hg_2Cl_2 is slowly converted into $HgCl_2$.

Iodides, insoluble in water, are generally soluble in nitrohydrochloric acid, except AgI. Hg_2I_2, HgI_2, and Cu_2I_2 react slowly with nitrohydrochloric acid, the anion being oxidized to iodine and even to iodic acid (HIO_3).

Sulfides, insoluble in water, are generally soluble in nitrohydrochloric acid, except Ag_2S, which is converted to AgCl.

Sulfates, insoluble in water, are slightly soluble in nitrohydrochloric acid, except Hg_2SO_4 (which is oxidized to a mercuric salt and dissolves fairly readily) and Ag_2SO_4 (which precipitates as AgCl).

Carbonates, insoluble in water, are soluble in nitrohydrochloric acid, except Ag_2CO_3, which is converted to AgCl.

Oxalates, insoluble in water, are soluble in nitrohydrochloric acid, except $Ag_2C_2O_4$, which is converted to AgCl.

Phosphates, insoluble in water, are soluble in nitrohydrochloric acid, except Ag_3PO_4, which is converted to AgCl. Stannic phosphate dissolves less readily in nitrohydrochloric acid than in hydrochloric acid alone.

V. Comparison among the acids.

A general comparison of the action of hydrochloric acid, nitric acid and nitrohydrochloric acid as solvents for the different classes of materials insoluble in water, may be derived from the above statements.

(a) *Metals.*

Nitrohydrochloric acid is the most effective solvent for free metals, nitric acid next, and hydrochloric acid is least effective (though Al, Cr and Sn can be dissolved better in hydrochloric acid than in nitric acid).

(b) *Oxides and hydroxides.*

Except for Group I metals (whose oxides and hydroxides are converted to relatively insoluble chlorides by both hydrochloric and nitrohydrochloric acids), hydrochloric acid is the most effective solvent for oxides and hydroxides, nitrohydrochloric acid next, and nitric acid is least effective (though salt-forming oxides of Group I metals dissolve best in nitric acid). The higher oxides react fairly readily with hydrochloric acid, slowly with nitrohydrochloric acid and not effectively at all with nitric acid.

(c) *Salts.*

Except for Group I metals (whose salts are converted to relatively insoluble chlorides by both hydrochloric and nitrohydrochloric acids), and for the cases in which oxidation of cation or anion is an important factor in dissolving the salt, hydrochloric acid is the most effective solvent for the salts, nitrohydrochloric acid next and nitric acid is least effective.

APPENDIX

§323. **Reagents.** — For some years past the aqueous reagents for use in qualitative chemical analysis at the University of Michigan have been made up on the normality basis. Thus a normal solution of KOH should contain 56.1 grams of the compound per liter of solution; but the available solid usually contains about 10% of moisture, so it is directed to weigh out $56.1 \times \frac{10}{9}$, or 62.3 grams of the solid, dissolve in water, and dilute to 1 liter, for a normal solution. In the case of reagents that may be used either as precipitating agents or as oxidants or reductants, the normality is figured in terms of the precipitation reaction. Thus a normal solution of $K_2Cr_2O_7$ would contain $\frac{294.2}{4}$ grams per liter, since this reagent is used to precipitate metals as chromates, and the valence of the chromate radical is 2. For a reagent that is used solely as an oxidant or reductant the normality is figured in terms of that reaction. Thus $KMnO_4$ is used as an oxidant, commonly undergoing five units of reduction per molecule, therefore a normal solution would contain $\frac{158}{5}$ grams per liter.

In addition to reagents, there should be available a set of test solutions, which the student may use to become familiar with the analytical behavior of the various metals and acid radicals, or to check up on reagents which may be open to suspicion. These test solutions are made up on an empirical basis, the concentration of the solution being so adjusted that 1 cc. of the solution contains 10 mg. of the metal or non-metal under consideration. This is a solution of sufficient concentration so that 3–5 cc. will be ample to study an ordinary reaction, and the solution may easily be diluted tenfold or a hundred fold to cover the lower concentrations commonly encountered.

The solutions used by the assistant in preparing unknowns for analysis commonly contain 30 mg. of metal or non-metal per cc. Known volumes of these are placed in 60 cc. tincture bottles, the bottles then being filled with water (acid or alkali being added as necessary for particular ions).

Many of the salts are commercially available in more than one degree of hydration. Thus sodium carbonate may be had as the anhydrous salt, Na_2CO_3, as the monohydrate, $Na_2CO_3 \cdot H_2O$, and as the decahydrate, $Na_2CO_3 \cdot 10H_2O$. In the tables only one of the more common forms has been used as the basis of calculation. If one of the other hydrates is being used the quantities must be correspondingly modified. In case of doubt as to the actual composition of the basic material it may be necessary to resort to some type of quantitative analysis. If the anhydrous salt is

fairly stable, it may be possible to ignite a weighed portion of the salt to the anhydrous condition to determine the actual amount of water present. In other cases it may be easier to use some simple gravimetric or volumetric method to determine the percent of metal or non-metal present.

Acids	*Normality*
Acetic, conc. (sp. gr. 1.05, 99.5%)	17.4
Acetic, dil., 287 cc. of the conc. acid per liter	5.0
Hydrochloric, conc. (sp. gr. 1.18, 36%)	11.6
Hydrochloric, dil., 431 cc. of the conc. acid per liter	5.0
Nitric, conc. (sp. gr. 1.42, 72%)	16.2
Nitric, dil., 309 cc. of the conc. acid per liter	5.0
Sulfuric, conc. (sp. gr. 1.84, 96%)	36.0
Sulfuric, dil., 139 cc. of the conc. acid, pour carefully into 500 cc. H_2O, cool, and dilute to 1 liter	5.0

Bases	
Ammonium hydroxide, conc. (sp. gr. 0.90, 28.4% NH_3)	15.0
Ammonium hydroxide, dil., 333 cc. of conc. NH_4OH per liter	5.0
Barium hydroxide, $Ba(OH)_2 \cdot 8H_2O$, 63 g. per liter, satd. soln. (filter off $BaCO_3$ and protect from CO_2 of the air)	0.4
Calcium hydroxide, $Ca(OH)_2$, 1.5 g. per liter, satd. soln. (use some excess, filter off $CaCO_3$ and protect from CO_2 of the air)	0.04
Potassium hydroxide, KOH (90%), dissolve 311 g. of the sticks in water and dilute to 1 liter	5.0
Sodium hydroxide, NaOH (90%), dissolve 222 g. of the sticks in water and dilute to 1 liter	5.0

Special Liquids and Solutions

Acetone, CH_3COCH_3 (free from reductants for $KMnO_4$)

Aluminon solution, 1.0 g. of the ammonium salt of aurin tricarboxylic acid, dissolve in H_2O and dilute to 1 liter. (0.1% solution.)

Amyl alcohol, $C_5H_{11}OH$.

Carbon tetrachloride, CCl_4.

Dimethyl glyoxime, $C_4H_8N_2O_2$. Dissolve 10 g. in ethyl alcohol, and dilute with alcohol to 1 liter. (1% solution.)

Ether, $(C_2H_5)_2O$.

Fehling's solution:

A (blue part). Dissolve 34.7 g. of $CuSO_4 \cdot 5H_2O$ in water and dilute to 500 cc.

B (colorless part). Dissolve 173 g. of Rochelle salts and 50 g. of NaOH in water and dilute to 500 cc.

Mix equal amounts of the two parts in use.

Formaldehyde, CH_2O. Dilute 125 cc. of the concentrated reagent (40% solution) with water to 1 liter (5% solution).

Hydrogen peroxide, H_2O_2. Use the commercial 3% solution.

Magnesia mixture. Dissolve 52 g. of $MgCl_2 \cdot 6H_2O$ and 134 g. of NH_4Cl in water, add 350 cc. of conc. NH_4OH, and dilute to 1 liter. Use only the freshly filtered reagent.

Nessler's reagent. Dissolve 50 g. of KI in 50 cc. of water, add saturated $HgCl_2$ solution (60 g. per liter) in small amounts at a time, with shaking, until a slight permanent precipitate forms, then add 200 cc. of 5 *N* NaOH and dilute to 1 liter. Let settle, then draw off the clear liquid.

Solid Reagents

Aluminum, metal, Al. Smooth coarse turnings, or #8 or #12 wire.
Ammonium chloride, NH_4Cl.
Ammonium thiocyanate, NH_4CNS.
Borax, $Na_2B_4O_7 \cdot 10H_2O$.
Copper, metal. Wire or turnings (for Hg test).
Iron, metal. Powder (for Sn test).
Microcosmic salt, $NaNH_4HPO_4 \cdot 4H_2O$.
Potassium acid antimonate, KH_2SbO_4 (for Na test).
Potassium chlorate, $KClO_3$.
Potassium nitrate, KNO_3.
Potassium persulfate, $K_2S_2O_8$.
Sodium acid sulfate, $NaHSO_4$.
Sodium bicarbonate, $NaHCO_3$.
Stannic chloride, $SnCl_4 \cdot 5H_2O$ (for PO_4^{-3} removal).
Stannous chloride, $SnCl_2 \cdot 2H_2O$ (for As test).
Tin, metal, Sn. Foil (for Sb test).
Zinc, metal, Zn. 20 mesh.

Salt Solutions

Reagent	Normality
Ammonium acetate, $NH_4C_2H_3O_2$, dissolve 231 g. of the salt in water and dilute to 1 liter.	3 *N*
Ammonium carbonate, coml. salt is a mixture of NH_4HCO_3 and $NH_4NH_2CO_2$. Dissolve 157 g. of the salt in 400 cc. of 5 *N* NH_4OH and dilute to 1 liter.	4 *N*
Ammonium chloride, NH_4Cl, dissolve 268 g. of the salt in 900 cc. of water and dilute to 1 liter.	5 *N*
Ammonium molybdate, $(NH_4)_2MoO_4$ (the coml. salt is the para molybdate, $(NH_4)_6Mo_7O_{24}$), dissolve 42 g. of MoO_3 (85%) in a mixture of 70 cc. of conc. NH_4OH and 140 cc. of water; after solution is complete, add very slowly, with vigorous stirring, a mixture of 250 cc. of conc. HNO_3 and 500 cc. of water; then dilute to 1 liter.	0.5 *N*
Ammonium oxalate, $(NH_4)_2C_2O_4 \cdot H_2O$, dissolve 35.5 g. of the salt in water and dilute to 1 liter.	0.5 *N*
Ammonium sulfate, $(NH_4)_2SO_4$, dissolve 132 g. of the salt in water and dilute to 1 liter (conc. reagent, to ppt. Sr before testing for Ca).	2.0 *N*
Ammonium sulfate, $(NH_4)_2SO_4$, dissolve 6.6 g. of the salt in water and dilute to 1 liter (dilute reagent, to test for Sr in the presence of Ca).	0.1 *N*
Ammonium sulfide, yellow, $(NH_4)_2S_x$, treat 150 cc. of conc. NH_4OH with H_2S till saturated, keeping the solution cold; add 250 cc. of conc. NH_4OH and 10 g. of washed sulfur, shake to dissolve the latter and dilute to 1 liter. (On standing, the concentration of $(NH_4)_2S_2$ increases and that of $(NH_4)_2S$ and NH_4OH decreases).	$(NH_4)_2S_2$ = 0.6 *N* $(NH_4)_2S$ = 3.9 *N* NH_4OH = 1.5 *N*
Barium chloride, $BaCl_2 \cdot 2H_2O$, dissolve 61 g. of the salt in water and dilute to 1 liter.	0.5 *N*
Calcium chloride, $CaCl_2 \cdot 6H_2O$, dissolve 55 g. of the salt in water and dilute to 1 liter.	0.5 *N*
Calcium hypochlorite, $Ca(ClO)_2$ (65%), treat 50 g. of the salt with water and dilute to 1 liter. Filter or decant when ready to use the reagent.	1.0 *N*
Calcium sulfate, $CaSO_4 \cdot 2H_2O$, satd. soln., treat 3.0 g. of the salt with 1 liter of water, shake occasionally over a period of several hours, then filter or decant.	0.03 *N*
Cupric sulfate, $CuSO_4 \cdot 5H_2O$, dissolve 124.8 g. of the salt in water, add 2–3 cc. of H_2SO_4, and dilute to 1 liter. (Normality is calculated as an oxidant.)	0.5 *N*
Ferric chloride, $FeCl_3 \cdot 6H_2O$, dissolve 135.2 g. of the salt in water containing 50 cc. of 5 *N* HCl, and dilute to 1 liter. (Normality is calculated as an oxidant.)	0.5 *N*

Ferric sulfate, $Fe_2(SO_4)_3 \cdot 9H_2O$, dissolve 140.5 g. of the salt in sufficient 5 *N* H_2SO_4 to make 1 liter. (Normality is calculated as an oxidant.) — 0.5 *N*

Ferrous sulfate, $FeSO_4 \cdot 7H_2O$, dissolve 139 g. of the salt in water containing 50 cc. of 5 *N* H_2SO_4, and dilute to 1 liter. (Normality is calculated as a reductant.) — 0.5 *N*

Lead acetate, $Pb(C_2H_3O_2)_2 \cdot 3H_2O$, dissolve 95 g. of the salt in water and dilute to 1 liter. — 0.5 *N*

Magnesium uranyl acetate, to 100 g. of uranyl acetate, $UO_2(C_2H_3O_2)_2 \cdot 2H_2O$, add 100 g. of glacial acetic acid, stir, and add 400 cc. of water. To 300 g. of $Mg(C_2H_3O_2)_2 \cdot 4H_2O$ add 200 cc. of water. Heat both solutions to the boiling point, keeping them hot until both are practically clear, then pour the Mg solution into the other. Let cool slightly and dilute to 1 liter. Let stand over night and filter. — $UO_2(C_2H_3O_2)_2$ = 0.47 *N*; $Mg(C_2H_3O_2)_2$ = 2.8 *N*; $HC_2H_3O_2$ = 1.7 *N*

Mercuric chloride, $HgCl_2$, dissolve 68 g. of the salt in water and dilute to 1 liter. — 0.5 *N*

Potassium cyanide, KCN, dissolve 33 g. of the salt in water and dilute to 1 liter. — 0.5 *N*

Potassium dichromate, $K_2Cr_2O_7$, dissolve 36.8 g. of the salt in water and dilute to 1 liter. (Normality is calculated as precipitant.) — 0.5 *N*

Potassium ferricyanide, $K_3Fe(CN)_6$, dissolve 55 g. of the salt in water and dilute to 1 liter. — 0.5 *N*

Potassium ferrocyanide, $K_4Fe(CN)_6 \cdot 3H_2O$, dissolve 212 g. of the salt in water and dilute to 1 liter. (Concentrated reagent used to remove Ca in testing for Sr.) — 2.0 *N*

Potassium ferrocyanide, $K_4Fe(CN)_6 \cdot 3H_2O$, dissolve 53 g. of the salt in water and dilute to 1 liter. — 0.5 *N*

Potassium iodide, KI, dissolve 83 g. of the salt in water and dilute to 1 liter. — 0.5 *N*

Potassium permanganate, $KMnO_4$, dissolve 15.8 g. of the salt in water and dilute to 1 liter. After standing for several days syphon off the clear solution, or filter through a Gooch crucible or its equivalent. (Normality is calculated as an oxidant.) — 0.5 *N*

Potassium thiocyanate, KCNS, dissolve 49 g. of the salt in water and dilute to 1 liter. — 0.5 *N*

Silver nitrate, $AgNO_3$, dissolve 85 g. of the salt in water and dilute to 1 liter. — 0.5 *N*

Silver sulfate, Ag_2SO_4, dissolve 8 g. of the salt in 1 liter of water. This is essentially a saturated solution. — 0.05 *N*

Sodium acetate, $NaC_2H_3O_2 \cdot 3H_2O$, dissolve 408 g. of the salt in water and dilute to 1 liter. — 3.0 *N*

Sodium carbonate, Na_2CO_3, dissolve 159 g. of the salt in water and dilute to 1 liter. — 3.0 *N*

Sodium cobaltinitrite, $Na_3Co(NO_2)_6$, dissolve 67.3 g. of the salt in water and dilute to 1 liter. (Or the solution may be prepared as follows: Dissolve 48.5 g. of $Co(NO_3)_2 \cdot 6H_2O$ in 100–150 cc. of water; dissolve 81 g. of $NaNO_2$ in 100–150 cc. of water; mix the two solutions with stirring; add 19.5 cc. of glacial acetic acid, stir thoroughly, dilute to 1 liter, shake, let stand a few days and filter.) — 0.5 *N*

Sodium cyanide, NaCN, dissolve 24.5 g. of the salt in water and dilute to 1 liter. — 0.5 *N*

Sodium hypochlorite, NaClO, use the solution sold under the trade names Oxol, or Chlorox, at most grocery stores. — 1.0 *N*

Sodium sulfite, $Na_2SO_3 \cdot 7H_2O$, dissolve 63 g. of the salt in water and dilute to 1 liter. — 0.5 *N*

Stannous chloride, $SnCl_2 \cdot 2H_2O$, treat 56 g. of the salt with 100 cc. of conc. HCl, let stand over night, then dilute to 1 liter. — 0.5 *N*

Test Solutions

These solutions are made up in such a way that 1 cc. contains 10 mg. of the metal or non-metal. The test solutions for the metals are arranged in the order of the groups; those for the non-metals are arranged alphabetically, the various acid radicals of each non-metal being listed in the order of increasing oxidation-number of the non-metal.

Metal	Formula of dry salt	Grams of salt per liter of soln.	Special precautions in preparing the soln.
Lead	$Pb(NO_3)_2$	16.0	use 5 cc. of 5 *N* HNO_3
Mercury (ous)	$Hg_2(NO_3)_2 \cdot 2H_2O$	14.0	use 150 cc. of 5 *N* HNO_3
Silver	$AgNO_3$	15.8	
Mercury (ic)	$HgCl_2$	13.5	
	$Hg(NO_3)_2$	16.2	use 50 cc. of 5 *N* HNO_3
	$HgSO_4$	14.8	use 50 cc. of 5 *N* H_2SO_4
Bismuth	$BiCl_3$	15.1	dissolve in 400 cc. of 5 *N* HCl and dilute to 1 liter
	$Bi(NO_3)_3 \cdot 5H_2O$	23.2	dissolve in 500 cc. of *N* HNO_3 and dilute to 1 liter
Copper	$CuCl_2 \cdot 2H_2O$	26.8	use 5 cc. of 5 *N* HCl
	$Cu(NO_3)_2 \cdot 3H_2O$	38.0	use 5 cc. of 5 *N* HNO_3
	$CuSO_4 \cdot 5H_2O$	39.3	use 5 cc. of 5 *N* H_2SO_4
Cadmium	$CdCl_2 \cdot 2H_2O$	19.4	use 5 cc. of 5 *N* HCl
	$Cd(NO_3)_2 \cdot 4H_2O$	27.4	use 5 cc. of 5 *N* HNO_3
	$3\ CdSO_4 \cdot 8H_2O$	22.8	use 5 cc. of 5 *N* H_2SO_4
Arsenic (ous)	As_2O_3	13.2	dissolve in hot water containing 15–20 cc. of 5 *N* HCl, and dilute to 1 liter
	$K_4As_2O_5$	25.8	
(ic)	As_2O_5	15.3	dissolve in hot water, adding a little HCl if necessary to form a clear solution, then dilute to 1 liter
	KH_2AsO_4	24.0	
Antimony (ous)	$SbCl_3$	18.7	dissolve in 400 cc. of 5 *N* HCl and dilute to 1 liter
(ic)	$SbCl_5$	24.5	dissolve in 500 cc. of 5 *N* HCl and dilute to 1 liter
Tin (ous)	$SnCl_2 \cdot 2H_2O$	19.0	treat the salt with 100 cc. of conc. HCl, let stand over night, then dilute to 1 liter. Filter if necessary
(ic)	$SnCl_4 \cdot 5H_2O$	29.5	dissolve in 400 cc. of 5 *N* HCl and dilute to 1 liter

Metal	Formula of dry salt	Grams of salt per liter of soln.	Special precautions in preparing the soln.
Iron (ous)	$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	70.3	use 25 cc. of 5 *N* H_2SO_4
(ic)	$FeCl_3 \cdot 6H_2O$	48.4	use 50 cc. of 5 *N* HCl
	$Fe(NO_3)_3 \cdot 9H_2O$	72.4	use 50 cc. of 5 *N* HNO_3
Aluminum	$AlCl_3 \cdot 6H_2O$	89.5	use 25 cc. of 5 *N* HCl
	$Al(NO_3)_3 \cdot 7\frac{1}{2}H_2O$	129.0	use 25 cc. of 5 *N* HNO_3
	$Al_2(SO_4)_3 \cdot 18H_2O$	123.5	use 25 cc. of 5 *N* H_2SO_4
Chromium (ic)	$CrCl_3 \cdot 6H_2O$	51.2	use 50 cc. of 5 *N* HCl
	$Cr(NO_3)_3 \cdot 9H_2O$	77.0	use 50 cc. of 5 *N* HNO_3
	$Cr_2(SO_4)_3 \cdot 18H_2O$	68.9	use 50 cc. of 5 *N* H_2SO_4
(ate)	K_2CrO_4	37.3	
	$K_2Cr_2O_7$	28.3	
Cobalt	$CoCl_2 \cdot 6H_2O$	40.4	use 25 cc. of 5 *N* HCl
	$Co(NO_3)_2 \cdot 6H_2O$	49.4	use 25 cc. of 5 *N* HNO_3
	$CoSO_4 \cdot 7H_2O$	47.7	use 25 cc. of 5 *N* H_2SO_4
Nickel	$NiCl_2 \cdot 6H_2O$	40.5	use 25 cc. of 5 *N* HCl
	$Ni(NO_3)_2 \cdot 6H_2O$	49.5	use 25 cc. of 5 *N* HNO_3
	$NiSO_4 \cdot 6H_2O$	44.8	use 25 cc. of 5 *N* H_2SO_4
Manganese (ous)	$MnCl_2 \cdot 4H_2O$	36.0	use 5 cc. of 5 *N* HCl
	$Mn(NO_3)_2 \cdot 6H_2O$	52.3	use 5 cc. of 5 *N* HNO_3
	$MnSO_4 \cdot 2H_2O$	34.0	use 5 cc. of 5 *N* H_2SO_4
(permanganate)	$KMnO_4$	28.8	
(manganate)	K_2MnO_4		place 28.8 g. of $KMnO_4$ in a 1 liter casserole, add 125 g. of KOH, and 100 cc. of water, cover with a watch glass and heat carefully until no further evolution of O_2 takes place. Cool, dissolve in water, and dilute to 1 liter.
Zinc	$ZnCl_2$	20.8	
	$Zn(NO_3)_2$	29.0	
	$ZnSO_4 \cdot 7H_2O$	44.0	
Barium	$BaCl_2 \cdot 2H_2O$	17.8	
	$Ba(NO_3)_2$	19.0	
Strontium	$SrCl_2 \cdot 6H_2O$	30.4	
	$Sr(NO_3)_2$	24.2	
Calcium	$CaCl_2 \cdot 2H_2O$	36.7	
	$Ca(NO_3)_2 \cdot 4H_2O$	58.9	
Magnesium	$MgCl_2 \cdot 6H_2O$	83.6	use 5 cc. of 5 *N* HCl
	$Mg(NO_3)_2 \cdot 6H_2O$	105.4	use 5 cc. of 5 *N* HNO_3
	$MgSO_4 \cdot 7H_2O$	101.4	use 5 cc. of 5 *N* H_2SO_4

Metal	Formula of dry salt	Grams of salt per liter of soln.	Special precautions in preparing the soln.
Sodium	$NaCl$ $NaNO_3$ Na_2SO_4	25.4 35.2 30.9	
Potassium	KCl KNO_3 K_2SO_4	19.1 25.9 22.3	
Ammonium	NH_4Cl NH_4NO_3 $(NH_4)_2SO_4$	29.7 44.4 36.1	

Non-Metals

Non-metal	Formula of dry salt	Grams of salt per liter of soln.	Special precautions in preparing the soln.
Bromine (Bromide)	KBr	14.9	
Carbon (oxalate) (carbonate)	$(NH_4)_2C_2O_4 \cdot H_2O$ $Na_2CO_3 \cdot 10H_2O$	59.2 238.5	
Chlorine (chloride) (chlorate)	NH_4Cl KCl $NaCl$ $KClO_3$	15.1 21.0 16.5 34.6	
Iodine (iodide) (iodate)	KI KIO_3	13.1 16.9	
Nitrogen (nitrate)	KNO_3 $NaNO_3$	72.2 60.7	
Phosphorus (phosphate)	$(NH_4)_2HPO_4$ $Na_2HPO_4 \cdot 12H_2O$	42.6 115.6	
Sulfur (sulfide)	Na_2S		Saturate 62.5 cc. of 5N NaOH with H_2S, add 62.5 cc. more of 5N NaOH, and dilute to 1 liter
(sulfite) (sulfate)	$Na_2SO_3 \cdot 7H_2O$ $(NH_4)_2SO_4$ K_2SO_4 Na_2SO_4	79.0 41.3 54.4 44.4	

§324. Grouping of the Metals. Remove each group before testing for the next.

<table>
<tr><td colspan="6">Add HCl to the cold, acid solution until pptn. is complete. Filter, wash.</td></tr>
<tr><td rowspan="5">Precipitate: Group I</td><td colspan="5">Make filtrate 0.25 N with HCl, treat with H_2S, and filter. Make filtrate 3–4 N with HCl, treat with H_2S, filter, and wash.</td></tr>
<tr><td rowspan="4">Precipitate: Group II</td><td colspan="4">Boil out H_2S, oxidize Fe^{++}, make 3–4 N with NH_4Cl, heat, add slight excess of NH_4OH, filter, and wash.</td></tr>
<tr><td rowspan="3">Precipitate Group III</td><td colspan="3">Add moderate excess of NH_4OH, treat with H_2S, filter and wash.</td></tr>
<tr><td rowspan="2">Precipitate: Group IV</td><td colspan="2">Remove excess NH_4^+, add NH_4OH, heat, add $(NH_4)_2CO_3$, filter, and wash.</td></tr>
<tr><td>Precipitate: Group V</td><td>Filtrate: Group VI</td></tr>
<tr>
<td>Lead
§§57, 62–65
$PbCl_2$ · · · white
Mercury
§§58, 62–64, 66, 67
Hg_2Cl_2 · · · white
Silver
§§59, 62–64, 66, 68
AgCl · · · white</td>
<td>Mercury
§§58, 80–83, 96, 97
HgS · · · black
Lead
§§57, 80–83, 96–99
PbS · · · black
Bismuth
§§76, 80–83, 96–101
Bi_2S_3 · · · black
Copper
§§77, 80–83, 96–103
CuS · · · black
Cadmium
§§78, 80–83, 96–103
CdS · · · yellow
Arsenic
§§69, 80–83, 85–88
As_2S_3, As_2S_5 · · · yellow
Antimony
§§70, 80–83, 85, 86, 89, 90
Sb_2S_3, Sb_2S_5 · · · orange
Tin
§§71, 80–83, 85, 86, 89, 90
SnS · · · brown
SnS_2 · · · yellow</td>
<td>Iron
§§126, 128–131
$Fe(OH)_3$ · · · red brown
Chromium
§§125, 128–131
$Cr(OH)_3$ · · · green
Aluminum
§§124, 128–131
$Al(OH)_3$ · · · white</td>
<td>Cobalt
§§132, 138–141
CoS · · · black
Nickel
§§133, 138–141
NiS · · · black
Manganese
§§134, 138, 139, 142, 143
MnS · · · pink
Zinc
§§135, 138, 139, 142, 143
ZnS · · · white</td>
<td>Barium
§§186, 191, 192
$BaCO_3$ · · · white
Strontium
§§187, 191, 192
$SrCO_3$ · · · white
Calcium
§§188, 191, 192
$CaCO_3$ · · · white</td>
<td>Magnesium
§§193, 211a, 212
Sodium
§§205, 211a, 213, 214
Potassium
§§205, 211a, 213, 214
Ammonium
§§207, 211a, 215, 215a</td>
</tr>
</table>

Table of Solubilities

	Silver	Lead	Mercurous	Mercuric	Cupric	Bismuth	Cadmium	Stannous	Stannic	Antimonous	Aluminum	Chromium	Ferrous	Ferric	Cobalt	Nickel	Manganese	Zinc	Barium	Strontium	Calcium	Magnesium	Potassium	Sodium	Ammonium
Acetate	2,b	1	3,b	1	1	1	1	1	1		1	1,h	1	1,h	1	1	2	1	1	1	1	1	1	1	1
Arsenate	5,b	5,b	4,b	5,b	5,b	5,b			5,b	5,b	5,b	4,b		5,b	5,b	5,b	4,b	5,b	4,b	3,b	4,b	4,b	1	1	1
Arsenite	4,b	4,b	4,b	5,b	5,b					5,b				4,b	5.b	5,b	4,b			3,b		1	1	1	1
Borate	4,b	4,b					4,b	4,b													3,b	4,b	1	1	1
Bromide	5,d	3,b	5,c	3,c	1	1,h	1	1,h	1,h	1,h	1,h	1,h	1	1,h	1	1	1	1	1	1	1	1	1	1	1
Carbonate	4,a	5,a	4,b	5,b	4,a	5,b	4,a						4,b		5,a	4,a	4,a	4,a	4,a	4,a	4,a	4,a	1	1	1
Chlorate	1	1		1	1	1	1				1	1										1	1	1	1
Chloride	5,d	2,b	5,c	2	1	1,h	1	1,h	1,h	1,h	1,h	1,h	1	1,h	1	1	1	1	1	1	1	1	1	1	1
Chromate	4,b	5,b	3,b	3,b	2,b	4,b						4,b		1	4,b	4,b		3,b	5,b	3,b	3,b	1	1	1	1
Cyanide	5,d	3,b		1			2,b						5,b		5,b	4,b	4,b	4,b	1	1	1	1	1	1	1
Ferricyanide	4,d	4,b			5,d	5,d	5						5,d	1	5,d	5,d	5,d					1	1	1	1
Ferrocyanide	3,d	5,b			5,d	5,d	5	4	4				5,d	5,d	5,d	5,d	5	5,d	3	1	1	1	1	1	1
Fluoride	1	4,b	2,b	2,b	4,b	1	3	1	1	1	3,h	4,b	3	4,h	2,b	2,b	3,b	2,b	3,b	4,b	4,b	4,b	1	2	1
Iodate	4,b	4,d	4	4	3	4	3								3			3	4,d			1	1	1	2
Iodide	5,d	4,c	5,c	5,c		4,b	1	3,b	2,b	3,b	1,h	1,h	1		1	1	1	1	1	1	1	1	1	1	1
Nitrate	1	1,h	1,h	1,h	1	1,h	1			1,h	1,h	1,h	1	1,h	1	1	1	1	1	1	1	1	1	1	1
Oxalate	4,b	5,b	5,b	5,b	4,b	4,b	4,b				4,b	3	4,b	1	5,b	5,b	4,b	5,b	4,b	4,b	5,b	4,b	1	2	2
Oxide (hydroxide)	4,a	4,a	5,b	5,a	5,a	5,b	5,a	5,b	5,b	4,b	5,b	5,b	4,b	5,b	5,b	5,b	5,a	5,a	2,a	3,a	3,a	5,a	1	1	1
Phosphate	5,b	5,b	5,b	5,b	5,b	5,b	5,b		5,b		5,b	5,b	4,b	5,b	5,b	5,b	5,b	5,b	5,b	5,b	4,b	4,b	1	1	1
Silicate		5,b					5,a				5,d	5,b	5,b	5,b	5,b	5,b	5,b	5,b	5,b	5,b	5,b	5,b	1	1	
Sulfate	3,b	4,d	4,c	2,h	1	1,h	1	1,h	1,h	1,h	1,h	1,h	1	1,h	1	1	1	1	5,d	4,d	3,d	1	1	1	1
Sulfide	5,c	5,b		5,c	5,c	5,c	5,b	5,b	5,b	5,b			5,b	5,b	5,c	5,c	5,a	5,b	2,a		3,a		1	1	1
Sulfite	4,b	4,b					3,b						4,b		4,b	4,b			4,b	4,b	4,b	2,b	1	1	1
Thiocyanate	5,d	2	5,c	4.d	4		3				1	1	1	1,h	1	1	1	1	1	1	1	1	1	1	1

§327. Problems in Synthesis

For the sake of a more thorough drill in the principles of oxidation and other reactions, a few problems are here given; a part of them the student should practically work at his table, but they are chiefly designed for class exercises. Special care should be taken that a pure product be formed and that the ingredients be taken from the sources indicated. In each case the authority for every step in the process should be stated.

1. Silver oxide from metallic silver.
2. Mercuric bromide from mercurous chloride and sodium bromide.
3. Chromic chloride from potassium chromate and hydrochloric acid.
4. Arsenic acid from potassium arsenite.
5. Potassium arsenate from arsenious oxide and potassium hydroxide.
6. Lead nitrate from lead chloride and potassium nitrate.
7. Mercurous nitrate from mercuric chloride and sodium nitrate.
8. Mercurous oxide from mercuric oxide.
9. Mercuric bromide from metallic mercury and potassium bromide.
10. Lead nitrate from lead dioxide and potassium nitrate.
11. Lead chromate from lead hydroxide and chromium hydroxide.
12. Barium chromate from chrome alum and barium carbonate.
13. Mercuric chromate from mercuric sulfide and chromium hydroxide.
14. Chromium sulfate from potassium dichromate and zinc sulfide.
15. Phosphoric acid from sodium phosphate.
16. Phosphorus from calcium phosphate.
17. Lead iodate from sodium iodide and lead sulfide.
18. Silver iodate from silver chloride and iodine.
19. Ferric arsenate from ferrous sulfide and arsenious oxide.
20. Mercuric bromide from mercuric sulfide and sodium bromide.
21. Ammonium sulfate from ammonium chloride and sulfur.
22. Sodium chloride from commercial salt.
23. Phosphorus from sodium phosphate.
24. Lead sulfide from trilead tetroxide and ferrous sulfide.
25. Ferrous sulfate from ferric oxide and sulfuric acid.
26. Ammonium hydroxide from potassium nitrate.
27. Cadmium sulfate from cadmium phosphate and ferrous sulfide.
28. Mercurous nitrate from mercuric sulfide and nitric acid.
29. Barium sulfate from potassium thiocyanate and barium chloride.
30. Mercurous chloride from mercuric oxide and sodium chloride.
31. Sodium iodate from potassium iodate and sodium chloride.
32. Sodium phosphate from calcium phosphate and sodium chloride.
33. Strontium nitrate from sodium nitrate and strontium sulfate.
34. Potassium sulfate from potassium nitrate and sulfur.
35. Barium sulfate from barium chloride and zinc sulfide.
36. Potassium permanganate from manganese dioxide and potassium nitrate.
37. Arsenious chloride from lead arsenate and sodium chloride.
38. Potassium chromate from potassium nitrate and lead chromate.
39. Potassium iodide from potassium chloride and iodine.
40. Barium chlorate from sodium chloride and barium nitrate.
41. Arsenious sulfide from arsine and ferrous sulfide.
42. Copper sulfate from copper sulfide.
43. Silver nitrite from silver chloride and sodium nitrate.
44. Cuprous chloride from metallic copper and sodium chloride.
45. Manganous carbonate from manganese peroxide and sodium carbonate.
46. Manganous pyrophosphate from manganese peroxide and ammonium phosphate.
47. Lead arsenate from lead sulfide and arsenious oxide.
48. Bismuth subnitrate from metallic bismuth and nitric acid.
49. Barium perchlorate from sodium chloride and barium hydroxide.
50. Lead iodate from metallic lead and iodine.

§328. Chemical Equivalence in Reactions

Since many of the calculations in analytical chemistry are based upon formulas of compounds and upon equations for chemical reactions, the introductory course in chemical analysis usually includes considerable practice in the writing of correct formulas and in the balancing of equations. This is a valuable part of the training of the student who is making an initial attempt to see a little below the surface of the subject of chemistry. Yet in this work it is equally important that the limitations as well as the usefulness of chemical formulas and balanced equations be emphasized. For, after all, chemical formulas and balanced equations represent chiefly only the reiteration of one's belief in two fundamental laws of chemistry; namely, the laws of definite proportions and of conservation of mass. If the atomic weights of the various elements are given, a chemical formula makes it possible to calculate the percentage composition of the compound, or an equation makes it possible to calculate the ratio by weight in which reagents interact and products are formed. But the chemical formula tells nothing of the physical or chemical properties of a compound, nor does an equation tell anything of the readiness with which a reaction takes place, or the special conditions of temperature, concentration, or proportionate amounts of reagents necessary to make the reaction an effective one. Obviously, these latter are important matters for one who is actually working with chemical substances; therefore it is necessary to maintain an interest in reactions which extends considerably beyond the writing of chemical formulas and the balancing of equations.

The important principle involved in the construction of chemical formulas is that the radicals must be joined in equivalent proportions. Thus, univalent radicals combine with (a) other univalent radicals in the ratio of 1 : 1, (b) bivalent radicals in the ratio of 2 : 1, (c) tervalent radicals in the ratio of 3 : 1, etc. Bivalent radicals combine with other bivalent radicals in the ratio of 1 : 1, with tervalent radicals in the ratio of 3 : 2, etc. From this, the rule for writing formulas for normal salts is sometimes stated: The least common multiple of the valences of the two ions, divided by the valence of each ion, gives the numbers to be used as subscripts to show the ratio in which the two ions are combined in the formula of the normal salt. Aluminum ion has a valence of three, while sulfate ion has a valence of two. The least common multiple of these two numbers is 6. This number, divided by the valences of the two ions separately, yields 2 as the subscript for aluminum ion and 3 for the sulfate ion. The formula is then written, $Al_2(SO_4)_3$.

The rule is sometimes stated in the following form without offering an explanation of its derivation: In writing the formula for a normal salt, place the two radicals adjacent to each other and insert as subscript for

the positive radical the valence of the negative radical, and as a subscript for the negative radical the valence of the positive radical. The number 1 need not be inserted. Further, if the two subscripts are both divisible by some small whole number, they are thus reduced to lower terms, except when the molecular weight is known to be a multiple of the simplest formula, in which case the correct molecular formula is retained.

It will be noted that this rule implies a previous knowledge of the valences of the ions, and even then, it covers only those salts which contain one kind of positive ion combined with one kind of negative ion. For " mixed salts " (acid salts, basic salts, and double salts in general), this rule merely indicates that the sum of the valences of the positive radicals (each valence multiplied by the subscript for the radical) must equal the sum of the valences of the negative radicals. Thus, in the basic lead carbonate, $Pb_3(OH)_2(CO_3)_2$, the total valence of three lead radicals is 6, and the total valence of two hydroxyl radicals and two carbonate radicals is 6. In alum, $KAl(SO_4)_2$, the total valence of one potassium radical and one aluminum radical is 4, and the total valence of two sulfate radicals is 4. Obviously, there is nothing about the valences of the radicals that will indicate the ratio in which different positive radicals or negative radicals will be combined in a mixed salt. Such matters are determined by the specific properties of the two radicals and occasionally by the conditions of formation of the given compound. Kendall and Sloan[1] in studying the solubility of lead chloride in several other chloride solutions, reported the existence of such double salts as $KCl{\cdot}2PbCl_2$ and $CaCl_2{\cdot}PbCl_2$. It is evident that no simple valence relationship will explain the diversity of these two formulas. These differences are bits of the specific information about chemical substances that have not been adequately organized as yet by rules or generalizations. They must be known in order to write the formulas of mixed salts correctly; but if they are given, along with the valences of the individual radicals, it is a simple matter to write the formula that will satisfy all the requirements. Thus the formula for white lead may be written if the information is available that this is a basic carbonate of lead, that the lead and carbonate ions each have a valence of 2 while the hydroxyl ion has a valence of 1, and, finally, that the carbonate and hydroxyl radicals are present in the ratio of 1 : 1. The valence of lead being 2, while the sum of the valences of one hydroxyl and one carbonate radical is 3, the least common multiple of these two numbers is 6. Therefore three lead radicals will be combined with two each of hydroxyl and carbonate radicals, and the formula may be written, $Pb_3(OH)_2(CO_3)_2$.

Similarly, in complex salts (which differ only in degree from double salts, there being no sharp dividing line between the two) there are no simple valence rules to apply in determining the composition of the complex radical. Thus, potassium argenticyanide has the formula $KAg(CN)_2$,

[1] Kendall and Sloan, *J. Am. Ch. Soc.*, **47**, 2317 (1925).

potassium nickelocyanide, $K_2Ni(CN)_4$, and potassium ferrocyanide, $K_4Fe(CN)_6$. In the first two cases the metals are present in the ratio of one equivalent of potassium to one of the other metal; but in the last case it is two equivalents of potassium to one of iron. It is evident that in such cases one cannot determine the formula from the various valences of the simple ions from which the complex salt is derived, although such a formula must satisfy the valence rule given above. On the contrary, there must be available, from experimental study or authoritative reference, data that will show the composition of the complex ion before the formula can be written with assurance.

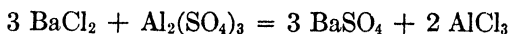
In writing equations to represent the proportions in which reagents interact and products are formed, the same principle is available as in the writing of formulas of normal salts, namely, the reagents interact with each other in equivalent proportions. That is, if two reagents interact with each other, the coefficients required for the balanced equation must be such that the two reagents will be used in the ratio of one equivalent of one to one of the other. If there is available some simple way of determining the number of equivalents represented by one molecule of each reagent it should be easy to write the equation. Thus, if one molecule of reagent *A* contains 2 equivalents, while one molecule of reagent *B* contains 3 equivalents, the least number of equivalents of these two that could be brought together in correct proportions for complete reaction, without using partial molecules, would be 6 (the least common multiple of 2 and 3). But if one molecule of *A* contains 2 equivalents, three molecules would be required to supply 6 equivalents. In the same way, two molecules of *B* would be required to supply 6 equivalents. Therefore the ratio by molecules in which *A* and *B* would interact would be 3 : 2. The difficulty, of course, is in determining the number of equivalents represented by the individual molecules of the reagents.

For reasons that will appear later, it is convenient to divide equations into two general classes, those not involving oxidation-reduction, and those that do involve oxidation-reduction. Typically, the latter are more complex than the former and so will be dealt with after the others have been considered.

EQUATIONS NOT INVOLVING OXIDATION-REDUCTION

The most common type of reaction not involving oxidation-reduction is metathesis, or interchange of radicals. This is the type of reaction represented by neutralization of sulfuric acid with sodium hydroxide, the precipitation of cupric ferrocyanide by the action of potassium ferrocyanide on cupric sulfate, or the dissolving of zinc sulfide in hydrochloric acid. In such cases the number of equivalents represented by one molecule of the

reagent is equal to the valence of either the positive or negative radical of the compound multiplied by its subscript. One molecule of sulfuric acid represents two equivalents since it contains 2 univalent hydrogen radicals (or 1 bivalent sulfate radical). One molecule of ferric sulfate, $Fe_2(SO_4)_3$, represents 6 equivalents, since it contains 2 tervalent ferric radicals (or 3 bivalent sulfate radicals). For a double salt, such as alum, $KAl(SO_4)_2$, obviously the number of equivalents represented by a molecule will be the sum of the equivalents of positive radical (K = 1, Al = 3) or of negative radical (2 bivalent sulfate radicals equal 4 equivalents). In writing the equation for the reaction of $BaCl_2$ with $Al_2(SO_4)_3$, since one molecule of the first reagent represents 2 equivalents and one molecule of the second reagent represents 6 equivalents, the least common multiple of these two numbers being 6, the reagents will interact in the ratio of 3 molecules of $BaCl_2$ to 1 of $Al_2(SO_4)_3$. The products will be 3 $BaSO_4$ and 2 $AlCl_3$.

$$3\ BaCl_2 + Al_2(SO_4)_3 = 3\ BaSO_4 + 2\ AlCl_3$$

There are other types of reaction not involving oxidation-reduction in which the relationship is more complex. Three groups of these reactions occur frequently enough so that they may well be considered in some detail at this time. These are the reactions involving (1) complex ammonia salts, (2) amphoteric hydroxides, and (3) other complex salts (cyanides, iodides, etc.). In order to write equations for these reactions intelligently, it is necessary to have something of an appreciation of the general nature of the products formed.

Complex ammonia salts, in aqueous solution, are strong electrolytes with the ammonia intimately associated with the metal in the complex ion. In forming such ions the essential material supplied by the reagent ammonium hydroxide is not the ammonium ion or hydroxyl ion, but molecular ammonia. In the combining of metallic ion with molecular ammonia no simple valence relationship is available to establish the ratio in which the two interact. The examination of formulas based on analytical studies leads to the following statement, covering the reactions in aqueous solution with the usual concentration of NH_4OH: Each metallic ion combines with a number of molecules of NH_3 equal to twice its valence in forming a complex ion. This rule covers the cases of Ag, Cu, Cd and Zn. Cobalt forms complex ions which contain from four to six molecules of ammonia per atom of cobalt. On this basis one might arbitrarily represent the reaction with the formula, $Co(NH_3)_4^{++}$, with the mental reservation that the composition is less definite than in the other cases mentioned. Nickel, however, departs still more from the above rule, in that the stable complex ion contains six molecules of ammonia to one atom of nickel. From this it will be seen that the principle of chemical equivalence cannot be applied to such cases merely from examination of the valences of the substances

entering into combination with each other. On the contrary, the equivalence relationship must be determined by an examination of the formula of the product formed.

In the case of metals having amphoteric hydroxides, the situation is somewhat similar, except that the reaction involving the dissolving of the hydroxide in acid or base is a neutralization reaction to which the elementary equivalence idea applies. Thus, in the dissolving of lead hydroxide, $Pb(OH)_2$, in nitric acid, the main reaction is $H^+ + OH^- = H_2O$, so the fact that one molecule of lead hydroxide supplies two hydroxyl radicals while one molecule of nitric acid supplies only one hydrogen ion means that the equation requires two molecules of nitric acid to one of lead hydroxide. In the dissolving of lead hydroxide in sodium hydroxide it would appear that the same reasoning should apply. The formula of plumbous acid, H_2PbO_2, indicates two hydrogen radicals per molecule to react with hydroxyl ion, therefore one would expect the equation to require two molecules of sodium hydroxide to one of plumbous acid. That is the form in which the equation is usually written, i.e., $H_2PbO_2 + 2\ NaOH = Na_2PbO_2 + 2\ H_2O$. The formulas of the other amphoteric hydroxides are also commonly rearranged in acid form by putting the hydrogen first: $Al(OH)_3 = H_3AlO_3$, $Zn(OH)_2 = H_2ZnO_2$, etc. The equations are then written by assuming that all the hydrogen reacts with hydroxyl radical. It is interesting, however, to note that certain lines of study suggest that in most cases the dissolving of the amphoteric hydroxide takes place with neutralization of only one hydrogen ion from the molecule. Thus the equation for the dissolving of zinc hydroxide in sodium hydroxide would read, $Zn(OH)_2 + NaOH = NaHZnO_2 + H_2O$.

The following data cover the common amphoteric hydroxides and the formulas of the anions obtained as they dissolve in NaOH:

$Pb(OH)_2$ PbO_2^{--}	$Sn(OH)_2$ SnO_2^{--}	$SnO(OH)_2$ SnO_3^{--}	$Sb(OH)_3$ SbO_2^-
$SbO(OH)_3$ SbO_4^{-3}	$Cr(OH)_3$ $H_2CrO_3^-$ (CrO_2^-)	$Al(OH)_3$ $H_2AlO_3^-$ (AlO_2^-)	$Zn(OH)_2$ $HZnO_2^-$

From these it will be evident that if one is writing the equation for the conversion of lead ion to plumbite ion (as in the reaction of lead nitrate with excess of sodium hydroxide, or the dissolving of lead sulfate in potassium hydroxide), a total of four hydroxyl radicals will be required for each lead ion — two to correspond to the conversion of lead ion to lead hydroxide, and two more to correspond to the change from $Pb(OH)_2$ to PbO_2^{--}. For the change from stannic ion to stannate ion six hydroxyl ions would be re-

quired for each stannic ion — four to correspond to the formation of $SnO(OH)_2$ and two more for the change from $SnO(OH)_2$ to SnO_3^{--}. Each aluminum ion requires four hydroxyl ions for conversion to aluminate ion, and each zinc ion requires three hydroxyl ions for conversion to zincate ion. Or, if one is considering the reactions starting with the alkaline solution, it requires two hydrogen ions to convert one plumbite ion to lead hydroxide and two more to convert the lead hydroxide to lead ion. It requires two hydrogen ions to convert one stannate ion to stannic hydroxide, and four more to convert the stannic hydroxide to stannic ion. In the same way, it requires one hydrogen ion to convert aluminate ion to aluminum hydroxide, and three more to convert the hydroxide to aluminum ion. It is evident that in writing equations for these reactions the ratio by molecules in which the reagents interact is obtained from a consideration of the products formed rather than merely an examination of the formulas of the reagents used.

A similar situation exists in the reactions involving the formation or decomposition of complex anions. A few formulas will make this evident. (See Table 44.)

TABLE 44

COMPOSITION OF CERTAIN COMPLEX ANIONS

Metal	Valence	Complex ion	Reaction
Ag........	1	$Ag(CN)_2^-$	$AgCN + CN^-$
Cu........	1	$Cu(CN)_4^{-3}$	$CuCN + 3\ CN^-$
Cd........	2	$Cd(CN)_4^{--}$	$Cd(CN)_2 + 2\ CN^-$
Co........	2	$Co(CN)_6^{-4}$	$Co(CN)_2 + 4\ CN^-$
Hg........	2	HgI_4^{--}	$HgI_2 + 2\ I^-$
Bi........	3	BiI_4^-	$BiI_3 + I^-$
Sn........	4	SnS_3^{--}	$SnS_2 + S^{--}$
As........	5	AsS_4^{-3}	$\frac{1}{2}(As_2S_5 + 3\ S^{--})$

If one starts with silver ion, two cyanide ions are necessary to form one argenticyanide ion, while four cyanide ions are necessary to convert one cuprous ion to cuprocyanide ion. The other cases are equally obvious. Thus one molecule of $(NH_4)_2S$ is equivalent to one molecule of SnS_2, or two molecules of HCl would be sufficient to precipitate SnS_2 from one molecule of $(NH_4)_2SnS_3$; but it would take three molecules of $(NH_4)_2S$ to convert one molecule of $SnCl_4$ to $(NH_4)_2SnS_3$, and six molecules of HCl would be required to convert one molecule of $(NH_4)_2SnS_3$ to $SnCl_4$.

One more case, of importance analytically, may be mentioned to stress the variety of reactions that actually occur. Ammonium molybdate reacts with phosphoric acid to form $(NH_4)_3PO_4 \cdot 12MoO_3$, ammonium phosphomolybdate, a compound in which twelve molecules of molybdic anhydride are combined with one molecule of ammonium phosphate. Clearly there

are no obvious valence relationships from which such a formula might be predicted, therefore here, as in the other cases above, it is necessary to know the formula of the main product before one is justified in attempting to write an equation.

Some progress has been made in attempting to classify complex salts by assigning to the metals "co-ordination numbers" which represent the characteristic number of groups that will be found associated with the metal in a stable complex ion. This is a topic that should be discussed in some detail in an advanced course in inorganic chemistry, but the conclusions are sufficiently irregular to make it only moderately useful as a basis for predicting reactions.

In balancing equations for these reactions the following procedure is suggested:

(1) Write the formulas for the reagents and products in the form of a skeleton equation,

(2) Examine the formula of the main product — or any product more complex than the rest — to determine the reagents from which its parts are derived,

(3) Use coefficients for the corresponding reagents that will supply these parts in the ratio required by the formula of the product,

(4) If one of the reagents supplies parts for a second product, calculate the amount needed for this and add that amount to the coefficient obtained in (3),

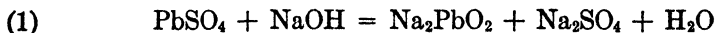
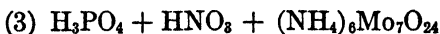
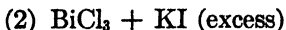
(5) Complete the balancing of the equation by inspection.

This procedure may be illustrated in balancing equations for the following reactions:

(1) $PbSO_4 + NaOH$ (excess)

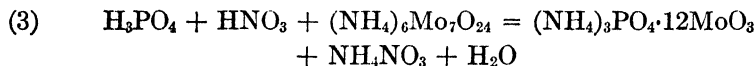
(2) $BiCl_3 + KI$ (excess)

(3) $H_3PO_4 + HNO_3 + (NH_4)_6Mo_7O_{24}$

(1) $$PbSO_4 + NaOH = Na_2PbO_2 + Na_2SO_4 + H_2O$$

The formula, Na_2PbO_2, requires 2 atoms of Na to 1 atom of Pb; and the formula, Na_2SO_4, requires 2 atoms of Na to 1 SO_4 radical. Since $PbSO_4$ is made up of 1 atom of Pb and 1 SO_4 radical, 1 molecule of $PbSO_4$ will react with 4 molecules of NaOH, forming 1 molecule of Na_2PbO_2 and 1 of Na_2SO_4. The 4 atoms of H from the 4 molecules of NaOH, plus the 2 atoms of O not used in the Na_2PbO_2, are accounted for in 2 molecules of H_2O. The balanced equation reads: $PbSO_4 + 4\ NaOH = Na_2PbO_2 + Na_2SO_4 + 2\ H_2O$.

(2) $$BiCl_3 + KI = KBiI_4 + KCl$$

The formula, $KBiI_4$, requires 4 atoms of iodine to 1 atom of Bi; and the formula, KCl, requires 1 atom of K to 1 atom of Cl. Since 1 molecule of $BiCl_3$ contains 1 atom of Bi and 3 atoms of Cl, while 1 molecule of KI contains 1 atom each of K and I; 1 molecule of $BiCl_3$ will react with 4 molecules of KI, forming 1 molecule of $KBiI_4$ and 3 molecules of KCl. The balanced equation reads: $BiCl_3 + 4\ KI = KBiI_4 + 3\ KCl$.

$$(3) \qquad H_3PO_4 + HNO_3 + (NH_4)_6Mo_7O_{24} = (NH_4)_3PO_4 \cdot 12MoO_3 + NH_4NO_3 + H_2O$$

The formula, $(NH_4)_3PO_4 \cdot 12MoO_3$, indicates that the reagents H_3PO_4 and $(NH_4)_6Mo_7O_{24}$ must supply P and Mo in the ratio of 1 atom of P to 12 atoms of Mo. The simplest ratio by molecules that will do this is 7 molecules of H_3PO_4 to 12 of $(NH_4)_6Mo_7O_{24}$. This would be sufficient to form 7 molecules of the product, $(NH_4)_3PO_4 \cdot 12MoO_3$. Twelve molecules of $(NH_4)_6Mo_7O_{24}$ contain 72 NH_4 radicals, of which 21 are used in 7 $(NH_4)_3PO_4 \cdot 12MoO_3$. The balance will be accounted for by considering that 51 molecules of NH_4NO_3 will be formed. This will require 51 molecules of HNO_3. The 51 atoms of H from the HNO_3, plus 21 atoms of H from 7 H_3PO_4, will be accounted for by using 36 as the coefficient of the product H_2O. The balanced equation reads: $7\ H_3PO_4 + 51\ HNO_3 + 12\ (NH_4)_6Mo_7O_{24} = 7\ (NH_4)_3PO_4 \cdot 12\ MoO_3 + 51\ NH_4NO_3 + 36\ H_2O$.

Before turning to oxidation-reduction equations, it may be well to emphasize, once more, the fact that the balanced equation tells little of the readiness with which a reaction takes place or the conditions necessary to make it effective. The reaction between Ag^+ and CN^- takes place readily with so slight an excess of CN^- that this forms the basis for an accurate volumetric method for CN^-. On the other hand, $Zn(OH)_2$ is not appreciably soluble in 0.1 *N* NaOH solution, and in dissolving Sb_2S_3 in $(NH_4)_2S_x$, a considerable excess of a moderately concentrated reagent is required.

EQUATIONS INVOLVING OXIDATION-REDUCTION

In attempting to balance equations involving oxidation-reduction, the principle discussed earlier still applies; namely, the reagents interact with each other in equivalent proportions. In oxidation-reduction processes there will always be a reagent undergoing oxidation and one undergoing reduction. Oxidation cannot take place without an accompanying reduction, nor reduction without an accompanying oxidation. In such a system the reagent undergoing oxidation is called the reducing agent, or reductant, and the reagent undergoing reduction is called the oxidizing agent, or oxidant. The problem is to determine the numbers of equivalents represented by one molecule of the oxidant and of the reductant respectively, and then to assign coefficients to these two reagents such that there will be

the same number of equivalents of oxidant as of reductant. The balancing of the equation may then be completed fairly easily by inspection. To determine the number of equivalents represented by one molecule of the oxidant or reductant it is necessary to compare the formula of the reagent with the product to which it is reduced or oxidized. There are several systems commonly employed in making such a comparison, each having its advocates. Three of these are used widely enough to justify being presented in outline form. They are called (1) the direct comparison method, (2) the oxidation-number method and (3) the ion-electron method.

The direct comparison method is based upon the older definitions of oxidation and reduction: *Oxidation* is the addition of oxygen or its equivalent to an element or a compound, or the removal of hydrogen or its equivalent from a compound. *Reduction* is the removal of oxygen or its equivalent from a compound, or the addition of hydrogen or its equivalent to an element or a compound. The phrase, its equivalent, as applied to oxygen means other negative elements (chlorine, sulfur, etc.) or negative groups (nitrate, sulfate, etc.). As applied to hydrogen, it means electropositive materials such as the metals and positive radicals. The terms, unit of oxidation, and unit of reduction, are used to indicate amounts of reaction in which one equivalent of material is being added or taken away. Thus, since K in combination is positive and has a valence of 1, if 1 atom of K is being added 1 unit of reduction is taking place. Or, since SO_4 in combination is negative and has a valence of 2, if 1 SO_4 group is being added 2 units of oxidation are taking place.

In the direct comparison method the formula of the oxidant is compared with that of the product to which it is reduced, and the formula of the reductant is compared directly with that of the product to which it is oxidized. The changes are indicated in terms of atoms or groups taken away from, or added to, the formula of the reagent to obtain the product. Setting down the number of units of oxidation or reduction involved in each atom or group added or taken away, these units of oxidation and of reduction are then totaled. If the number of units of reduction exceeds the number of units of oxidation, the compound is undergoing reduction, and the difference between the two totals for one molecule of the reagent shows the number of equivalents represented by one molecule of the reagent for that particular reaction. If the number of units of oxidation exceeds the number of units of reduction, the compound is undergoing oxidation, and the difference in the totals for one molecule of the reagent shows the number of equivalents represented by one molecule of the reagent for that particular reaction. The numbers of equivalents thus obtained serve as a direct basis for indicating the ratio by molecules in which the two reagents interact so far as oxidation-reduction is concerned.

The oxidation-number method is an outgrowth of the conception of oxidation and reduction as involving change in valence. The earlier definitions

along this line found it necessary to distinguish " positive " elements from " negative " elements. Thus, oxidation is increase in valence in the case of a positive element, but decrease in valence in the case of a negative element. Reduction — the reverse of oxidation — is decrease in valence in the case of a positive element, but increase in valence in the case of a negative element. These definitions were simplified by combining the character of the element with its valence and considering the valence to be positive or negative as the case might be in particular compounds, and zero in the case of the free element.[1] On this basis Cu in CuO has a valence of $+2$, while S in H_2S has a valence of -2. A change from Cu° to CuO would involve a change in valence of the Cu from 0 to $+2$, and a change from H_2S to S° would involve a change in valence of the S from -2 to 0. From this point of view, there has been an increase in valence in both of these reactions, from 0 to $+2$, and from -2 to 0. With this particular conception of valence understood, oxidation becomes increase in valence, and reduction, decrease in valence.

There are obvious objections to the use of the term valence in this way. Further, there are serious questions as to the validity of many of the structural formulas that have been used in the past — and still are frequently encountered — from which the valences of various elements in compounds are obtained. The thing of fundamental importance is the state of oxidation of the elements in particular compounds, oxidation and reduction being processes that involve changes in the state of oxidation of particular atoms or groups of atoms. It seems worth while to use another name than valence to indicate these states of oxidation. For want of a better term, the name oxidation-number has been used for some time at the University of Michigan. The *oxidation-number* of an element is a number which, applied to an element in a particular compound, shows the amount of oxidation or reduction involved in converting one atom of the element from the free state to the compound in question. If the element is uncombined, it is assigned an oxidation-number of 0. If oxidation is required to change it to the compound in question, the oxidation-number is positive and equal to the number of units of oxidation which one atom of the element undergoes in the change. If reduction is required to change it to the compound in question, the oxidation-number is negative and equal to the number of units of reduction which one atom of the element undergoes. Thus, the oxidation-numbers of Cu and S, both as free elements, would be 0. If one atom of Cu is changed to CuO, it undergoes 2 units of oxidation; therefore

[1] This idea was presented originally by O. C. Johnson, *Ch. News*, **42**, 51 (1880), who used the terms positive and negative bonds to picture the way in which the positive and negative elements were held in combination in compounds. It is interesting to note that the later development of the concept that a positive element is one which loses an electron readily, while a negative element is one which gains an electron readily, indicated a mechanism in distinct harmony with the suggestions of Johnson.

the oxidation-number of Cu in CuO is +2. If one atom of S is changed to H_2S, it undergoes 2 units of reduction; therefore the oxidation-number of S in H_2S is −2. This leads to a definition of oxidation as increase in oxidation-number and reduction as decrease in oxidation-number.

The rules for determining oxidation-numbers are fairly simple.

1. Free elements have an oxidation-number of zero.
2. Hydrogen in combination normally has an oxidation-number of +1.
3. Oxygen in combination normally has an oxidation-number of −2.
4. The oxidation-number of a compound (the sum of the oxidation-numbers of the individual elements, each multiplied by the number of atoms of the element in one molecule) is zero.
5. The oxidation-number of a radical is the same as its valence, with the corresponding plus or minus sign added.

A brief discussion of these rules will help to make their application apparent. The first one is sufficiently obvious to need no further comment.

The second rule is based on the general acceptance of hydrogen as the standard for measuring valence and equivalence. It is interesting to note, however, that in the rare case of hydrides of the more electropositive metals, it is more consistent with the other chemical facts to consider the metal as positive and the hydrogen negative. In hydrides of the less electropositive metals (metals below H in the electromotive series), such as AsH_3 and SbH_3, the metal is considered as negative and the hydrogen positive, just as in the hydrides of phosphorus and nitrogen (PH_3, NH_3, N_2H_4).

The third rule covers the fact that most of the oxygen compounds may be considered as related to H_2O, with the substitution of other positive element or elements for the hydrogen. An exception must be made, however, in compounds of the peroxide type (hydrogen peroxide and the peroxy-acids). It is obvious that for hydrogen peroxide, H_2O_2, rules 2 and 3 are in direct conflict, and an exception must be made to one or the other. Hydrogen peroxide may be considered as H_2O, to which an atom of oxygen has been added, increasing the oxidation-number of the hydrogen from +2 to +4; or it may be considered as O_2 to which two atoms of hydrogen have been added, decreasing the oxidation-number of the two atoms of oxygen from 0 to −2. So far as balancing equations is concerned, either of these points of view is adequate, since both of them, logically used, would lead to the same result. But the peculiar chemical behavior of these peroxides, as compared with such compounds as MnO_2 (in relation to MnO), etc., has led to a general acceptance of the second of the two points of view, namely, that the oxygen in these cases is in a state of oxidation intermediate between that of free oxygen and the ordinary oxide condition. Thus the two

atoms of oxygen in H_2O_2 are assigned a total oxidation-number of -2 to balance the $+2$ of the two atoms of hydrogen.

The fourth rule is derived from the fact that oxidation and reduction in a particular reaction always occur in equivalent amounts. If, then, the uncombined elements are assigned the oxidation-number zero, and they enter into combination with each other in equivalent proportions in forming the compound, the amount of oxidation that part of the elements undergo will equal the amount of reduction that the other elements undergo; therefore the sum of the oxidation-numbers of the various atoms in a molecule will be zero. From this, it will be evident that when two molecules combine to form a new molecule, the oxidation-numbers of the elements in the new compound may be considered to remain the same as they were. Thus, in the combining of NH_3 with HCl to form NH_4Cl, the N, H, and Cl retain their oxidation-numbers of -3, $+1$, and -1, per atom, respectively. In the combining of $FeSO_4$ with NO to form $FeSO_4 \cdot NO$ (in the brown-ring test for a nitrate), the Fe, S, N, and O, may all be considered to have the same oxidation-numbers that they had in the separate molecules. And in the combining of molecules with ions to form complex ions, the oxidation-numbers of the various elements do not change. Thus, molecular ammonia combines with silver ion to form the complex silver-ammonia ion, $Ag(NH_3)_2^+$, in which the Ag, N and H, all have the same oxidation-numbers as before combination took place. The same is true for such complex ions as thiostannate ion, SnS_3^{--}, cuprocyanide ion, $Cu(CN)_4^{-3}$, etc., formed by combination of molecular material with negative ions.

The fifth rule is derived from considerations similar to those just discussed. The fact that the radical is found only in combination with other radicals of opposite types is due to the fact that in the combining of elements to form radicals, the oxidation and reduction processes are not represented in equivalent amounts. If, from the elements combined, oxidation appears to have taken place to a greater extent than reduction, the radical will be positive and have a valence equal to the discrepancy between units of oxidation and units of reduction represented by the atoms of the various elements present. If reduction appears to have taken place to a greater extent than oxidation, the radical will be negative and have a valence equal to the discrepancy between units of oxidation and units of reduction. This rule, taken in connection with rules 2 and 3, usually makes it simple to calculate the oxidation numbers of accessory elements in radicals. Thus, in ammonium radical, the fact that its oxidation-number is $+1$ and that it contains one atom of nitrogen and four atoms of hydrogen (the latter being assigned an oxidation-number of $+1$ for each atom), means that the oxidation-number of the nitrogen is -3. Occasionally an element may appear in a radical (or compound) with two or more atoms in different states of oxidation. In such a case it is sufficient to use the radical (or molecule) as a unit and calculate merely the sum of the oxida-

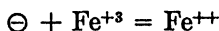
tion-numbers of the different atoms of the element without attempting to assign values to the individual atoms. Thus, in thiosulfate ion, $S_2O_3^{--}$, the two atoms of S have a total oxidation-number of +4, which may be used for calculating the change which the thiosulfate undergoes (in being oxidized to tetrathionate, $S_4O_6^{--}$, for example, in which four atoms of sulfur have a total oxidation-number of +10), without being concerned with the fact that the two atoms of sulfur individually may be assigned such diverse numbers as +6 and −2 (according to the point of view that thiosulfate radical is the same as sulfate radical with one atom of oxygen replaced by sulfur). This same principle applies in considering such compounds as Pb_3O_4 (3 atoms of Pb have a total oxidation-number of +8), NH_4NO_3 (2 atoms of N = +2), and $HC_2H_3O_2$ (2 atoms of C = 0). Sometimes in a radical two elements may be present, both of which are known to appear in various compounds with different states of oxidation. In such a case there is no direct way to determine the values to be assigned in the individual cases. Accessory information as to the behavior of such radicals with other reagents may make it desirable to assign particular values to these elements, but in the absence of such information, it is still possible to handle oxidation-reduction reactions involving such radicals by comparing the sum of the oxidation-numbers of the two elements in the reagent with the sum of the oxidation-numbers of the same numbers of atoms of these elements in the products. As a case in point, consider the compound potassium cyanide, KCN. Carbon is known to vary in oxidation-number from +4 (in CO_2) to −4 (in CH_4), while nitrogen is known to vary from +5 (in HNO_3) to −3 (in NH_3). Obviously, all that is known about the oxidation-numbers of the C and N in the cyanide radical is that the sum of the two is −1. This might be accounted for by assigning sets of values all the way from C = +2 and N = −3, to C = −4 and N = +3. It is interesting, as a matter of additional knowledge of chemical behavior, to know that KCN, in aqueous solution, slowly hydrolyzes to potassium formate, $KCHO_2$, and ammonium hydroxide; on the basis of which the first of the above alternatives is considered to be correct. But it is not necessary to know this, or to know the range of possibilities of oxidation-numbers of carbon and nitrogen in order to handle oxidation-reduction equations effectively. Thus KCN, used as a fusion reagent to reduce certain oxides to the metal, is oxidized to the cyanate, KCNO. The sum of the oxidation-numbers of C and N in KCN is −1, and in KCNO is +1, therefore two units of oxidation are involved in the change from cyanide to cyanate. Again, cyanide ion is oxidized by bromine to cyanogen bromide, CNBr. In CN^- the sum of the oxidation-numbers of the C and N is −1, while in CNBr it is +1, therefore two units of oxidation are involved per cyanide ion. Finally, in the titration of thiocyanate ion, CNS^-, with potassium permanganate, the products are HCN and K_2SO_4. In the thiocyanate ion, the sum of the oxidation-numbers of the C, N and S is −1,

while in the products it is $+5$ (-1 for C + N, and $+6$ for S), therefore six units of oxidation are involved per thiocyanate ion.

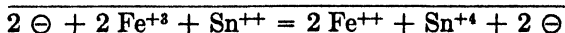
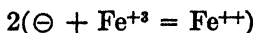
In balancing an oxidation-reduction equation by the oxidation-number method, the reductant is compared with the product to which it is oxidized to discover which elements are common to both; these are assigned their oxidation-numbers for the two states of oxidation; and the difference in oxidation-number per atom, multiplied by the number of such atoms in the molecule of the reagent, indicates the number of equivalents represented by one molecule of the reductant. In a similar way, by comparison of the oxidant with the product to which it is reduced, the change in oxidation-number of particular atoms will indicate the number of equivalents in one molecule of the oxidant. These numbers then determine the ratio by molecules in which the two reagents interact so far as oxidation-reduction is involved.

The ion-electron method of balancing oxidation-reduction equations is based on the newer conception that oxidation involves loss of electrons while reduction involves gain of electrons, the unit change in each case being a change of 1 electron. This method is limited to reactions of the ionic type in aqueous solution. It divides the reaction into two partial equations representing the oxidation and the reduction respectively. Besides the ions supplied by the reagents directly, water, hydrogen ion and hydroxyl ion are considered as available reagents, to be used as needed in constructing partial equations that will have the same number of atoms of each element on each side of the equation. Each partial equation is then examined for the extent of its failure to balance electrically. Thus, in the reaction of $FeCl_3$ with $SnCl_2$, the partials would read, $Fe^{+3} = Fe^{++}$, and $Sn^{++} = Sn^{+4}$. In the first case, there is one more positive charge shown on the left than on the right. This is taken care of by adding 1 electron ($\ominus$) on the left side. The second equation has two more positive charges on the right side than on the left. This is taken care of by adding 2 $\ominus$ on the right. The two equations then read:

$$\ominus + Fe^{+3} = Fe^{++}$$

$$Sn^{++} = Sn^{+4} + 2\ \ominus$$

These partials are then multiplied by small whole numbers such as will cause the same numbers of electrons to be used up in one reaction as are liberated by the other. The two sets of partials thus obtained are added together to form the completed ionic equation.

$$2(\ominus + Fe^{+3} = Fe^{++})$$

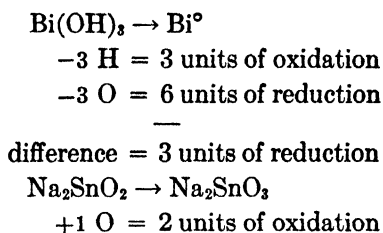
$$\underline{Sn^{++} = Sn^{+4} + 2\ \ominus}$$

$$2\ \ominus + 2\ Fe^{+3} + Sn^{++} = 2\ Fe^{++} + Sn^{+4} + 2\ \ominus$$

By cancelling the electrons from the two sides, the simple ionic equation is obtained, $2\ Fe^{+3} + Sn^{++} = 2\ Fe^{++} + Sn^{+4}$. It may be interesting to note that the extents of electrical divergence of the two partial equations may be used directly to determine the ratio in which the two partials must be taken to produce a balanced equation. Thus, the fact that the first partial above had an extra plus charge in the reagent, while the second partial had two extra plus charges in the product, would show that the two partials would be required in the ratio of 2 : 1.

To illustrate the three methods described above, several typical oxidation-reduction equations will be balanced by the different procedures.

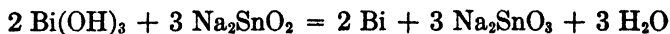
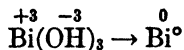
Reaction I. $Bi(OH)_3 + Na_2SnO_2 = Bi^\circ + Na_2SnO_3 + H_2O$.
The oxidant is $Bi(OH)_3$, being reduced to Bi.
The reductant is Na_2SnO_2, being oxidized to Na_2SnO_3.

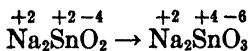
Direct comparison:

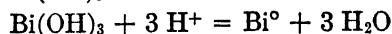
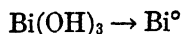
$$Bi(OH)_3 \rightarrow Bi^\circ$$
$$-3\ H = 3 \text{ units of oxidation}$$
$$-3\ O = 6 \text{ units of reduction}$$
$$\text{difference} = 3 \text{ units of reduction}$$
$$Na_2SnO_2 \rightarrow Na_2SnO_3$$
$$+1\ O = 2 \text{ units of oxidation}$$

Since one molecule of $Bi(OH)_3$ undergoes 3 units of reduction, it represents 3 equivalents, and since one molecule of Na_2SnO_2 undergoes 2 units of oxidation, it represents 2 equivalents; therefore the reagents will interact in the ratio of 2 molecules of $Bi(OH)_3$ to 3 molecules of Na_2SnO_2. The balancing is completed by inspection, giving the equation:

$$2\ Bi(OH)_3 + 3\ Na_2SnO_2 = 2\ Bi + 3\ Na_2SnO_3 + 3\ H_2O$$

Oxidation-number:

$$\overset{+3}{Bi}(\overset{-3}{OH})_3 \rightarrow \overset{0}{Bi^\circ}$$

One atom of Bi changes in oxidation-number from +3 to 0, undergoing 3 units of reduction.

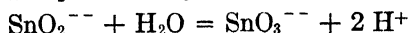
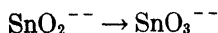
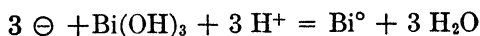
$$\overset{+2}{Na_2}\overset{+2}{Sn}\overset{-4}{O_2} \rightarrow \overset{+2}{Na_2}\overset{+4}{Sn}\overset{-6}{O_3}$$

One atom of Sn changes in oxidation-number from +2 to +4, undergoing 2 units of oxidation.

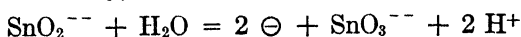
(The discussion of the procedure from this point on is the same as for the direct comparison method.)

Ion-electron:

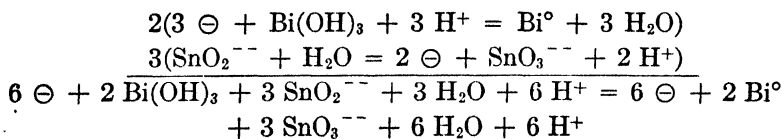
$$Bi(OH)_3 \rightarrow Bi^\circ$$
$$Bi(OH)_3 + 3\ H^+ = Bi^\circ + 3\ H_2O$$

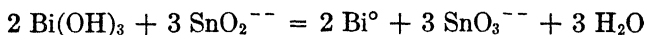
To balance electrically, add 3 ⊖ on the left side, thus:

$$3 \ominus + Bi(OH)_3 + 3\ H^+ = Bi^\circ + 3\ H_2O$$

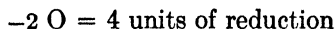
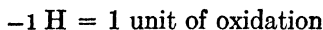
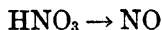
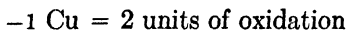
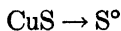
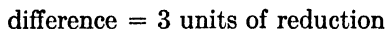
$$SnO_2^{--} \rightarrow SnO_3^{--}$$
$$SnO_2^{--} + H_2O = SnO_3^{--} + 2\ H^+$$

To balance electrically, add 2 ⊖ on the right side, thus:

$$SnO_2^{--} + H_2O = 2 \ominus + SnO_3^{--} + 2\ H^+$$

Since one molecule of $Bi(OH)_3$ uses 3 ⊖, and one stannite ion liberates 2 ⊖, the two partials will interact in the ratio of 2 : 3. By combining them in this way, the following result is obtained:

$$2(3 \ominus + Bi(OH)_3 + 3\ H^+ = Bi^\circ + 3\ H_2O)$$
$$3(SnO_2^{--} + H_2O = 2 \ominus + SnO_3^{--} + 2\ H^+)$$
$$6 \ominus + 2\ Bi(OH)_3 + 3\ SnO_2^{--} + 3\ H_2O + 6\ H^+ = 6 \ominus + 2\ Bi^\circ + 3\ SnO_3^{--} + 6\ H_2O + 6\ H^+$$

By cancelling, this equation is reduced to the simple form:

$$2\ Bi(OH)_3 + 3\ SnO_2^{--} = 2\ Bi^\circ + 3\ SnO_3^{--} + 3\ H_2O$$

Reaction II. $CuS + HNO_3 = Cu(NO_3)_2 + NO + S + H_2O$
The oxidant is HNO_3, being reduced to NO.
The reductant is CuS, being oxidized to S.

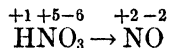
Direct comparison:

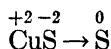
$$HNO_3 \rightarrow NO$$
$$-1\ H = 1 \text{ unit of oxidation}$$
$$-2\ O = 4 \text{ units of reduction}$$
$$\text{difference} = 3 \text{ units of reduction}$$
$$CuS \rightarrow S^\circ$$
$$-1\ Cu = 2 \text{ units of oxidation}$$

Since one molecule of HNO_3 undergoes 3 units of reduction and one molecule of CuS undergoes 2 units of oxidation, the two will interact with each other in the ratio of 3 molecules of CuS to 2 molecules of HNO_3. Further, since the product, $Cu(NO_3)_2$, requires 2 nitrate radicals for each atom of Cu, and the 3 molecules of CuS contain 3 atoms of Cu; therefore 6 more mole-

cules of HNO_3 will be required to balance the equation. The equation, completed by inspection, reads:

$$3\ CuS + 8\ HNO_3 = 3\ Cu(NO_3)_2 + 2\ NO + 3\ S^\circ + 4\ H_2O$$

Oxidation-number:

$$\overset{+1\,+5-6}{HNO_3} \rightarrow \overset{+2\,-2}{NO}$$

Nitrogen changes in oxidation-number from +5 to +2, which is 3 units of reduction.

$$\overset{+2\,-2}{CuS} \rightarrow \overset{0}{S}$$

Sulfur changes in oxidation-number from −2 to 0, which is 2 units of oxidation.

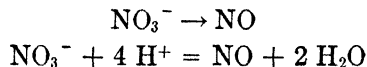
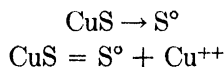
(The discussion from this point on is the same as for the direct comparison method.)

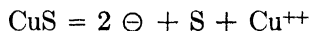
Ion-electron:

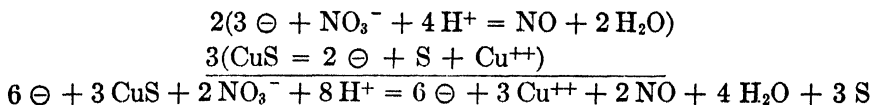
$$NO_3^- \rightarrow NO$$
$$NO_3^- + 4\ H^+ = NO + 2\ H_2O$$

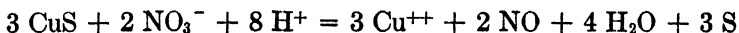
To balance electrically, add 3 $\ominus$ on the left side, i.e.,

$$3 \ominus + NO_3^- + 4\ H^+ = NO + 2\ H_2O$$

$$CuS \rightarrow S^\circ$$
$$CuS = S^\circ + Cu^{++}$$

To balance electrically, add 2 $\ominus$ on the right side, i.e.,

$$CuS = 2 \ominus + S + Cu^{++}$$

Since one nitrate ion uses 3 $\ominus$ while one molecule of CuS liberates 2 $\ominus$, the two partials will interact in the ratio of 2 : 3. By combining them in this ratio, the following result is obtained:

$$2(3 \ominus + NO_3^- + 4\ H^+ = NO + 2\ H_2O)$$
$$\underline{3(CuS = 2 \ominus + S + Cu^{++})}$$
$$6 \ominus + 3\ CuS + 2\ NO_3^- + 8\ H^+ = 6 \ominus + 3\ Cu^{++} + 2\ NO + 4\ H_2O + 3\ S$$

By cancelling, this equation is simplified to:

$$3\ CuS + 2\ NO_3^- + 8\ H^+ = 3\ Cu^{++} + 2\ NO + 4\ H_2O + 3\ S$$

Reaction III. $KMnO_4 + FeSO_4 + H_2SO_4 = MnSO_4 + K_2SO_4 + Fe_2(SO_4)_3 + H_2O$.

The oxidant is $KMnO_4$, being reduced to $MnSO_4$.

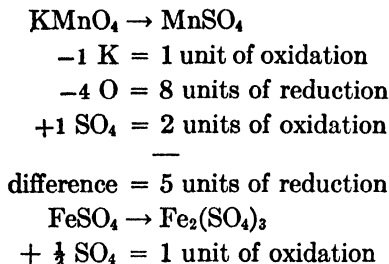
The reductant is $FeSO_4$, being oxidized to $Fe_2(SO_4)_3$.

Direct comparison:

$$KMnO_4 \rightarrow MnSO_4$$

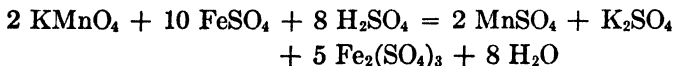
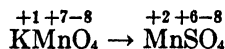
$$\begin{aligned} -1\ K &= 1 \text{ unit of oxidation} \\ -4\ O &= 8 \text{ units of reduction} \\ +1\ SO_4 &= \underline{2} \text{ units of oxidation} \\ \text{difference} &= 5 \text{ units of reduction} \end{aligned}$$

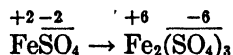
$$FeSO_4 \rightarrow Fe_2(SO_4)_3$$

$$+ \tfrac{1}{2}\ SO_4 = 1 \text{ unit of oxidation}$$

Since one molecule of $KMnO_4$ undergoes 5 units of reduction, and one molecule of $FeSO_4$ undergoes 1 unit of oxidation, the two will interact in the ratio of 1 molecule of $KMnO_4$ to 5 molecules of $FeSO_4$. Since the product, $Fe_2(SO_4)_3$, requires an even number of atoms of Fe, the numbers in the ratio, 1 : 5, are multiplied by 2, making 2 : 10. The numbers of molecules of $MnSO_4$, K_2SO_4, and $Fe_2(SO_4)_3$ required to account for the atoms of Mn, K, and Fe are calculated, and from these (minus the number of sulfate radicals supplied by the $FeSO_4$), the number of molecules of H_2SO_4 is obtained. Completing the balancing by inspection, the equation is obtained:

$$2\ KMnO_4 + 10\ FeSO_4 + 8\ H_2SO_4 = 2\ MnSO_4 + K_2SO_4 + 5\ Fe_2(SO_4)_3 + 8\ H_2O$$

Oxidation-number:

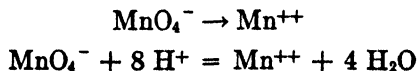
$$\overset{+1\,+7-8}{KMnO_4} \rightarrow \overset{+2\,+6-8}{MnSO_4}$$

Manganese changes in oxidation-number from +7 to +2, which is 5 units of reduction.

$$\overset{+2\,\underline{-2}}{Fe\overline{SO_4}} \rightarrow \overset{+6\quad\underline{-6}}{Fe_2\overline{(SO_4)}_3}$$

Fe changes in oxidation-number from +2 to +3 (1 atom of Fe = + 6/2 = +3), which is 1 unit of oxidation.

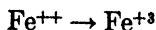
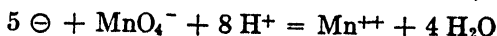
(The discussion from this point on is the same as in the direct comparison method.)

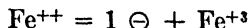
Ion-electron:

$$MnO_4^- \rightarrow Mn^{++}$$

$$MnO_4^- + 8\ H^+ = Mn^{++} + 4\ H_2O$$

To balance electrically, add 5 ⊖ on the left-hand side, i.e.,

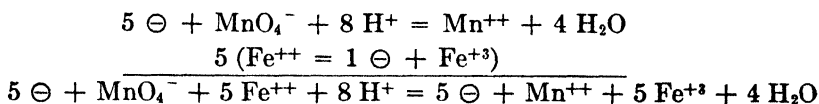
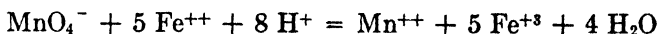
$$5 \ominus + MnO_4^- + 8\,H^+ = Mn^{++} + 4\,H_2O$$

$$Fe^{++} \rightarrow Fe^{+3}$$

To balance electrically, add 1 ⊖ on the right-hand side, i.e.,

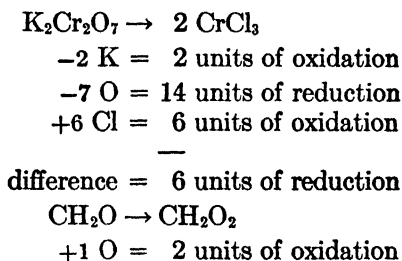
$$Fe^{++} = 1 \ominus + Fe^{+3}$$

Since one permanganate ion uses 5 ⊖ while one ferrous ion liberates 1 ⊖, the two partials will interact in the ratio of 1 : 5. By combining them in this ratio, the following result is obtained:

$$5 \ominus + MnO_4^- + 8\,H^+ = Mn^{++} + 4\,H_2O$$
$$5\,(Fe^{++} = 1 \ominus + Fe^{+3})$$
$$5 \ominus + MnO_4^- + 5\,Fe^{++} + 8\,H^+ = 5 \ominus + Mn^{++} + 5\,Fe^{+3} + 4\,H_2O$$

Cancelling, this becomes:

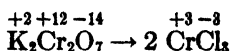
$$MnO_4^- + 5\,Fe^{++} + 8\,H^+ = Mn^{++} + 5\,Fe^{+3} + 4\,H_2O$$

Reaction IV. $K_2Cr_2O_7 + CH_2O + HCl = KCl + CrCl_3 + CH_2O_2 + H_2O$.
The oxidant is $K_2Cr_2O_7$, being reduced to $CrCl_3$.
The reductant is CH_2O, being oxidized to CH_2O_2.

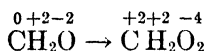
Direct comparison:

$$K_2Cr_2O_7 \rightarrow 2\,CrCl_3$$
$$-2\,K = 2 \text{ units of oxidation}$$
$$-7\,O = 14 \text{ units of reduction}$$
$$+6\,Cl = 6 \text{ units of oxidation}$$
$$\text{difference} = 6 \text{ units of reduction}$$
$$CH_2O \rightarrow CH_2O_2$$
$$+1\,O = 2 \text{ units of oxidation}$$

Since one molecule of $K_2Cr_2O_7$ undergoes 6 units of reduction, and one molecule of CH_2O undergoes 2 units of oxidation, the two will interact with each other in the ratio of 1 molecule of $K_2Cr_2O_7$ to 3 molecules of CH_2O. Accounting for the numbers of molecules of the KCl, $CrCl_3$ and CH_2O_2 formed, and of HCl required, by inspection, the balanced equation reads:

$$K_2Cr_2O_7 + 3\,CH_2O + 8\,HCl = 2\,KCl + 2\,CrCl_3 + 3\,CH_2O_2 + 4\,H_2O$$

Oxidation-number:

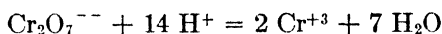
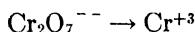
$$\overset{+2}{K_2}\overset{+12}{Cr_2}\overset{-14}{O_7} \rightarrow 2\,\overset{+3}{Cr}\overset{-3}{Cl_3}$$

Two atoms of Cr undergo a change in oxidation-number from +12 to +6 (+3 × 2), which is 6 units of reduction.

$$\overset{0\,+2-2}{CH_2O} \rightarrow \overset{+2+2\,-4}{C\,H_2O_2}$$

Carbon undergoes a change in oxidation-number from 0 to +2, which is 2 units of oxidation.

(The discussion from this point on is the same as in the direct comparison method.)

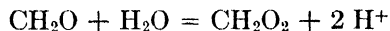
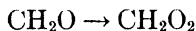
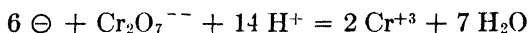
Ion-electron:

$$Cr_2O_7^{--} \rightarrow Cr^{+3}$$

$$Cr_2O_7^{--} + 14\ H^+ = 2\ Cr^{+3} + 7\ H_2O$$

To balance electrically, add 6 ⊖ on the left-hand side, thus,

$$6 \ominus + Cr_2O_7^{--} + 14\ H^+ = 2\ Cr^{+3} + 7\ H_2O$$

$$CH_2O \rightarrow CH_2O_2$$

$$CH_2O + H_2O = CH_2O_2 + 2\ H^+$$

To balance electrically, add 2 ⊖ on the right-hand side, thus,

$$CH_2O + H_2O = 2 \ominus + CH_2O_2 + 2\ H^+$$

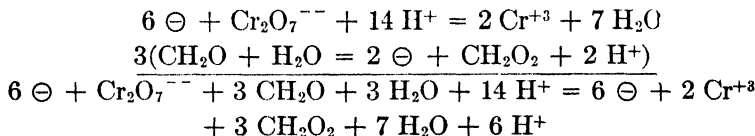
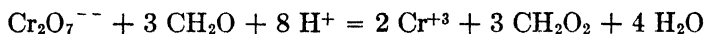
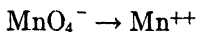
Since one dichromate ion uses 6 ⊖ and one molecule of CH_2O liberates 2 ⊖, the two partials will interact in the ratio of 1 : 3. By combining them in this ratio, the following result is obtained:

$$6 \ominus + Cr_2O_7^{--} + 14\ H^+ = 2\ Cr^{+3} + 7\ H_2O$$

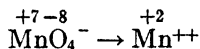
$$\underline{3(CH_2O + H_2O = 2 \ominus + CH_2O_2 + 2\ H^+)}$$

$$6 \ominus + Cr_2O_7^{--} + 3\ CH_2O + 3\ H_2O + 14\ H^+ = 6 \ominus + 2\ Cr^{+3} + 3\ CH_2O_2 + 7\ H_2O + 6\ H^+$$

By cancelling, this becomes:

$$Cr_2O_7^{--} + 3\ CH_2O + 8\ H^+ = 2\ Cr^{+3} + 3\ CH_2O_2 + 4\ H_2O$$

From the fact that the equations balanced by the first two methods were written in the molecular form, the impression may have been gained that these methods are not suited for handling ionic equations. To counteract such an impression it is only necessary to note that the plus and minus charges conventionally assigned to the ions can be included in comparing reagents with products.

$$
\begin{aligned}
MnO_4^- &\rightarrow Mn^{++} \\
-4\ O &= 8 \text{ units of reduction} \\
-1\ - &= 1 \text{ unit of oxidation} \\
+2\ + &= 2 \text{ units of oxidation} \\
\text{difference} &= 5 \text{ units of reduction}
\end{aligned}
$$

In the same way, in assigning oxidation-numbers, the sum of the values for the atoms in an ion must be equal to the valence of the ion and have the same sign.

$$\overset{+7\,-8}{MnO_4^-} \rightarrow \overset{+2}{Mn^{++}}$$

Mn changes from an oxidation-number of +7 to +2, which is 5 units of reduction.

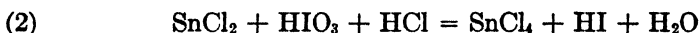
There is, of course, considerable basis for the argument that ionic equations represent the reactions with which one is actually dealing in the great majority of chemical changes in aqueous solution. But it must be remembered that ions can be handled as chemical substances only in the presence of an equivalent amount of oppositely charged ions. Further, in order to work intelligently with ionic reactions, it is necessary to have a considerable range of reasonably accurate information as to extents of dissociation of weak electrolytes and of complex ions, solubilities of compounds, and oxidizing or reducing strength of reagents under varying conditions. On this basis, in carrying out a permanganate titration, one may think of the reagent used as potassium permanganate, a salt essentially completely ionized in aqueous solution, a powerful oxidant in acid solution but distinctly milder in neutral or alkaline solution. Or, one may think of the reagent as permanganate ion, which can be had only in aqueous solution, accompanied by an equivalent amount of some positive ion such as potassium, the permanganate ion being a powerful oxidant in acid solution, but distinctly milder in neutral or alkaline solution. It is obvious that the difference between these two points of view is vanishingly small, and that any argument in favor of one rather than the other would probably be based on incomplete understanding of the one held in disrepute.

It will be observed in the cases cited that the various systems of balancing oxidation-reduction equations have this in common, that they involve an examination of the reductant in conjunction with the product to which it is oxidized, and of the oxidant in conjunction with the product to which it is reduced. The purpose is the same in all cases, namely, to determine the numbers of equivalents represented by the formulas of the two reagents so that the ratio in which they react with each other may be calculated. An examination of the procedure used in balancing the equations by the several methods, shows another interesting point, namely, all three systems

start with the assumption that one already knows what the oxidant is, what the reductant is, and the particular products to which they are respectively reduced and oxidized. But one actually needs a practical working knowledge of oxidation-reduction reactions in order to glance quickly through a list of reagents and products and sort out these various substances. None of the definitions of oxidation and reduction are so obvious that the beginning chemist who has committed a set of them to memory can immediately handle an oxidation-reduction reaction effectively. A considerable fund of chemical fact and theory is a necessary background for all of the definitions. Without this supplementary information, none of the definitions will work. Even with it available, the beginner finds it necessary to spend many hours in practice with a well assorted series of reactions before he develops reasonable facility in dealing with these cases. Further, after practice with particular reactions it is desirable to use a set of new reactions to test one's grasp of the fundamentals of the oxidation-reduction process (as distinct from having memorized a few reactions).

The following list of skeleton equations, with statements as to oxidation-reduction effects, includes a number of the more complex types of reactions.

(1) $$SnCl_2 + H_2SO_3 + HCl = SnCl_4 + H_2S + H_2O$$

The tin undergoes a change in oxidation-number from $+2$ to $+4$, or two units of oxidation per molecule of $SnCl_2$. The sulfur undergoes a change in oxidation-number from $+4$ to -2, or six units of reduction per molecule of H_2SO_3. Therefore, the reagents interact in the ratio of three molecules of $SnCl_2$ to one of H_2SO_3.

(2) $$SnCl_2 + HIO_3 + HCl = SnCl_4 + HI + H_2O$$

The tin undergoes a change in oxidation-number from $+2$ to $+4$, or two units of oxidation per molecule of $SnCl_2$. The iodine undergoes a change in oxidation-number from $+5$ to -1, or six units of reduction per molecule of HIO_3. Therefore, the two reagents interact in the ratio of three molecules of $SnCl_2$ to one of HIO_3.

(3) $$HMnO_4 + AsH_3 + H_2SO_4 = H_3AsO_4 + MnSO_4 + H_2O$$

The manganese undergoes a change in oxidation-number from $+7$ to $+2$, or five units of reduction per molecule of $HMnO_4$. The arsenic undergoes a change in oxidation-number from -3 to $+5$, or eight units of oxidation per molecule of AsH_3. Therefore, the reagents interact in the ratio of eight molecules of $HMnO_4$ to five molecules of AsH_3.

(4) $$As_4 + HNO_3 + H_2O = H_3AsO_4 + NO$$

The arsenic undergoes a change in oxidation-number from 0 to $+5$, or twenty units of oxidation (for 4 atoms of As) per molecule of As_4. The

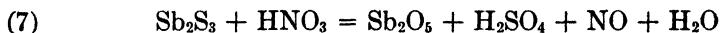
nitrogen undergoes a change in oxidation-number from +5 to +2, or three units of reduction per molecule of HNO_3. Therefore the two reagents interact in the ratio of three molecules of As_4 to twenty of HNO_3.

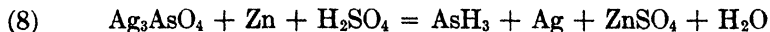
(5) $$Sb + HNO_3 = Sb_2O_5 + NO + H_2O$$

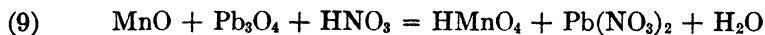
The antimony undergoes a change in oxidation-number from 0 to +5, or five units of oxidation per atom of Sb. The nitrogen undergoes a change in oxidation-number from +5 to +2, or three units of reduction per molecule of HNO_3. Therefore the reagents interact in the ratio of three atoms of Sb to five molecules of HNO_3. (These numbers are multiplied by two to supply an even number of atoms of Sb for Sb_2O_5.)

(6) $$H_2S + HNO_3 = H_2SO_4 + NO + H_2O$$

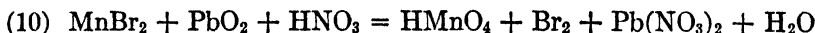
The sulfur undergoes a change in oxidation-number from −2 to +6, or eight units of oxidation per molecule of H_2S. The nitrogen undergoes a change in oxidation-number from +5 to +2, or three units of reduction per molecule of HNO_3. Therefore the reagents interact in the ratio of three molecules of H_2S to eight molecules of HNO_3.

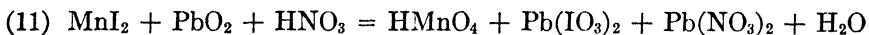
(7) $$Sb_2S_3 + HNO_3 = Sb_2O_5 + H_2SO_4 + NO + H_2O$$

The antimony undergoes a change in oxidation-number from +3 (per atom) to +5, and the sulfur undergoes a change in oxidation-number from −2 (per atom) to +6, or a total of twenty-eight units of oxidation (for 2 atoms of Sb and 3 atoms of S) per molecule of Sb_2S_3. The nitrogen undergoes a change in oxidation-number from +5 to +2, or three units of reduction per molecule of HNO_3. Therefore the two reagents interact in the ratio of three molecules of Sb_2S_3 to twenty-eight of HNO_3.

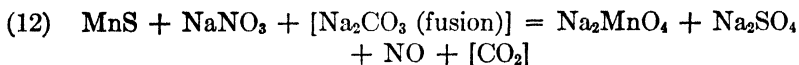
(8) $$Ag_3AsO_4 + Zn + H_2SO_4 = AsH_3 + Ag + ZnSO_4 + H_2O$$

The silver undergoes a change in oxidation-number from +1 (per atom) to 0, and the arsenic undergoes a change in oxidation-number from +5 to −3, or a total of eleven units of reduction (for 3 atoms of Ag and 1 atom of As) per molecule of Ag_3AsO_4. The zinc undergoes a change in oxidation-number from 0 to +2, or two units of oxidation per atom of Zn. Therefore the reagents interact in the ratio of two molecules of Ag_3AsO_4 to eleven atoms of Zn.

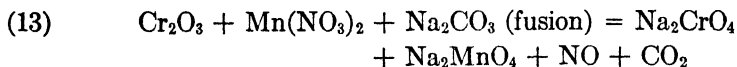
(9) $$MnO + Pb_3O_4 + HNO_3 = HMnO_4 + Pb(NO_3)_2 + H_2O$$

The manganese undergoes a change in oxidation-number from +2 to +7, or five units of oxidation per molecule of MnO. The lead undergoes a change in oxidation-number from +8 (the sum of the numbers for 3 atoms of Pb) to +6 (for 3 atoms of Pb), or two units of reduction per

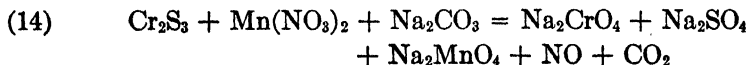
molecule of Pb_3O_4. Therefore the reagents interact in the ratio of two molecules of MnO to five molecules of Pb_3O_4.

(10) $MnBr_2 + PbO_2 + HNO_3 = HMnO_4 + Br_2 + Pb(NO_3)_2 + H_2O$

The manganese undergoes a change in oxidation-number from +2 to +7, and the bromine undergoes a change in oxidation-number from −1 to 0, or a total of seven units of oxidation (for 1 atom of Mn and 2 atoms of Br) per molecule of $MnBr_2$. The lead undergoes a change in oxidation-number from +4 to +2, or two units of reduction per molecule of PbO_2. Therefore the reagents interact in the ratio of two molecules of $MnBr_2$ to seven molecules of PbO_2.

(11) $MnI_2 + PbO_2 + HNO_3 = HMnO_4 + Pb(IO_3)_2 + Pb(NO_3)_2 + H_2O$

The manganese undergoes a change in oxidation-number from +2 to +7, and the iodine undergoes a change in oxidation-number from −1 to +5, or a total of seventeen units of oxidation (for 1 atom of Mn and 2 atoms of I), per molecule of MnI_2. The lead undergoes a change in oxidation-number from +4 to +2, or two units of reduction per molecule of PbO_2. Therefore the reagents interact in the ratio of two molecules of MnI_2 to seventeen molecules of PbO_2.

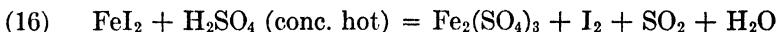
(12) $MnS + NaNO_3 + [Na_2CO_3 \text{ (fusion)}] = Na_2MnO_4 + Na_2SO_4 + NO + [CO_2]$

The manganese undergoes a change in oxidation-number from +2 to +6, and the sulfur undergoes a change in oxidation-number from −2 to +6, or a total of twelve units of oxidation per molecule of MnS. The nitrogen undergoes a change in oxidation-number from +5 to +2, or three units of reduction per molecule of HNO_3. Therefore the reagents interact in the ratio of one molecule of MnS to four molecules of $NaNO_3$.

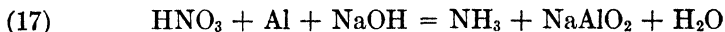
(13) $Cr_2O_3 + Mn(NO_3)_2 + Na_2CO_3 \text{ (fusion)} = Na_2CrO_4 + Na_2MnO_4 + NO + CO_2$

The chromium undergoes a change in oxidation-number from +3 to +6, or six units of oxidation (for 2 atoms of Cr) per molecule of Cr_2O_3. The manganese undergoes a change in oxidation-number from +2 to +6, but the nitrogen undergoes a change in oxidation-number from +5 to +2, or a total of two units of reduction (for 1 atom of Mn and 2 atoms of N) per molecule of $Mn(NO_3)_2$. Therefore the reagents interact in the ratio of one molecule of Cr_2O_3 to three molecules of $Mn(NO_3)_2$.

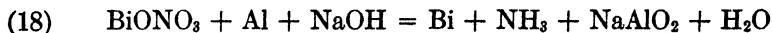
(14) $Cr_2S_3 + Mn(NO_3)_2 + Na_2CO_3 = Na_2CrO_4 + Na_2SO_4 + Na_2MnO_4 + NO + CO_2$

The chromium undergoes a change in oxidation-number from +3 to +6, and the sulfur undergoes a change in oxidation-number from −2 to +6, or a total of thirty units of oxidation (for 2 atoms of Cr and 3 atoms of S) per molecule of Cr_2S_3. The manganese undergoes a change in oxidation-number from +2 to +6, but the nitrogen undergoes a change in oxidation-number from +5 to +2, or a total of two units of reduction (for 1 atom of Mn and 2 atoms of N) per molecule of $Mn(NO_3)_2$. Therefore the reagents interact in the ratio of one molecule of Cr_2S_3 to fifteen molecules of $Mn(NO_3)_2$.

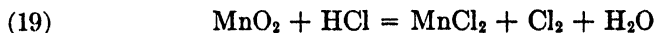
(15) $$Ag + HNO_3 = AgNO_3 + NO + H_2O$$

The silver undergoes a change in oxidation-number from 0 to +1, or one unit of oxidation per atom of Ag. The nitrogen undergoes a change in oxidation-number from +5 to +2, or three units of reduction per molecule of HNO_3. Therefore the reagents interact in the ratio of three atoms of Ag to one molecule of HNO_3, so far as oxidation-reduction is concerned. But three more molecules of HNO_3 are required to supply nitrate radical for the three atoms of Ag, so in the balanced equation, four molecules of HNO_3 are required altogether.

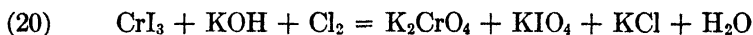
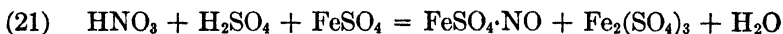
(16) $$FeI_2 + H_2SO_4 \text{ (conc. hot)} = Fe_2(SO_4)_3 + I_2 + SO_2 + H_2O$$

The iron undergoes a change in oxidation-number from +2 to +3, and the iodine undergoes a change in oxidation-number from −1 to 0, or a total of three units of oxidation (for 1 atom of Fe and 2 atoms of I) per molecule of FeI_2. The sulfur undergoes a change in oxidation-number from +6 to +4, or two units of reduction per molecule of H_2SO_4. Therefore the reagents interact in the ratio of two molecules of FeI_2 to three molecules of H_2SO_4.

(17) $$HNO_3 + Al + NaOH = NH_3 + NaAlO_2 + H_2O$$

The nitrogen undergoes a change in oxidation-number from +5 to −3, or eight units of reduction per molecule of HNO_3. The aluminum undergoes a change in oxidation-number from 0 to +3, or three units of oxidation per atom of Al. Therefore the reagents interact in the ratio of three molecules of HNO_3 to eight atoms of Al.

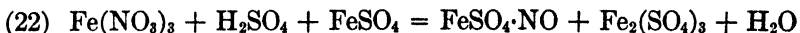
(18) $$BiONO_3 + Al + NaOH = Bi + NH_3 + NaAlO_2 + H_2O$$

The bismuth undergoes a change in oxidation-number from +3 to 0, and the nitrogen undergoes a change in oxidation-number from +5 to −3, or a total of eleven units of reduction (for 1 atom of Bi and 1 atom of N) per molecule of $BiONO_3$. The aluminum undergoes a change in oxidation-number from 0 to +3, or three units of oxidation per atom of Al. There-

fore the reagents interact in the ratio of three molecules of $BiONO_3$ to eleven atoms of Al.

(19) $$MnO_2 + HCl = MnCl_2 + Cl_2 + H_2O$$

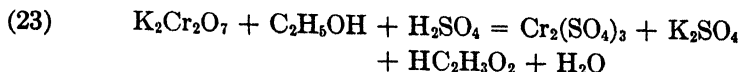
The manganese undergoes a change in oxidation-number from +4 to +2, or two units of reduction per molecule of MnO_2. The chlorine undergoes a change in oxidation-number from −1 to 0, or one unit of oxidation per molecule of HCl. Therefore the reagents interact in the ratio of one molecule of MnO_2 to two molecules of HCl, so far as oxidation-reduction is concerned. But two more molecules of HCl are required to supply chloride radical for the one atom of Mn, so in the balanced equation, a total of four molecules of HCl are used.

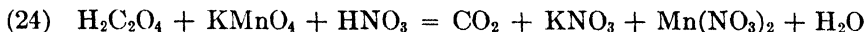
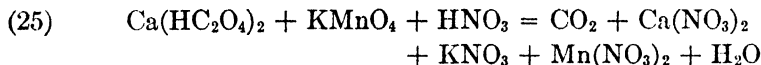
(20) $$CrI_3 + KOH + Cl_2 = K_2CrO_4 + KIO_4 + KCl + H_2O$$

The chromium undergoes a change in oxidation-number from +3 to +6, and the iodine undergoes a change in oxidation-number from −1 to +7, or a total of twenty-seven units of oxidation (for 1 atom of Cr and 3 atoms of I) per molecule of CrI_3. The chlorine undergoes a change in oxidation-number from 0 to −1, or two units of reduction (for 2 atoms of Cl) per molecule of Cl_2. Therefore the reagents interact in the ratio of two molecules of CrI_3 to twenty-seven molecules of Cl_2.

(21) $$HNO_3 + H_2SO_4 + FeSO_4 = FeSO_4 \cdot NO + Fe_2(SO_4)_3 + H_2O$$

The nitrogen undergoes a change in oxidation-number from +5 to +2, or three units of reduction per molecule of HNO_3. The iron undergoes a change in oxidation-number from +2 to +3 [in $Fe_2(SO_4)_3$], or one unit of oxidation per molecule of $FeSO_4$. Therefore the reagents interact in the ratio of one molecule of HNO_3 to three molecules of $FeSO_4$, so far as oxidation-reduction is concerned. But one more molecule of $FeSO_4$ is needed to combine with the NO, making a ratio of one to four, and these numbers must be multiplied by two to supply an even number of atoms of Fe for $Fe_2(SO_4)_3$.

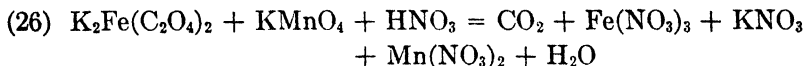
(22) $$Fe(NO_3)_3 + H_2SO_4 + FeSO_4 = FeSO_4 \cdot NO + Fe_2(SO_4)_3 + H_2O$$

The nitrogen undergoes a change in oxidation-number from +5 to +2, or nine units of reduction (for 3 atoms of N) per molecule of $Fe(NO_3)_3$. The iron undergoes a change in oxidation-number from +2 to +3 [in $Fe_2(SO_4)_3$], or one unit of oxidation per molecule of $FeSO_4$. Therefore the reagents interact in the ratio of one molecule of $Fe(NO_3)_3$ to nine molecules of $FeSO_4$, so far as oxidation-reduction is concerned. But three more molecules of $FeSO_4$ are needed to combine with the three molecules of

NO, so in the balanced equation a total of twelve molecules of $FeSO_4$ are used.

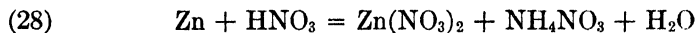
(23) $$K_2Cr_2O_7 + C_2H_5OH + H_2SO_4 = Cr_2(SO_4)_3 + K_2SO_4 + HC_2H_3O_2 + H_2O$$

The chromium undergoes a change in oxidation-number from +6 to +3, or six units of reduction (for 2 atoms of Cr) per molecule of $K_2Cr_2O_7$. The carbon undergoes a change in oxidation-number from −4 (the sum of the numbers for 2 atoms of C), to 0 (for 2 atoms of C), or four units of oxidation per molecule of C_2H_5OH. Therefore the reagents interact in the ratio of two molecules of $K_2Cr_2O_7$ to three molecules of C_2H_5OH.

(24) $$H_2C_2O_4 + KMnO_4 + HNO_3 = CO_2 + KNO_3 + Mn(NO_3)_2 + H_2O$$

The carbon undergoes a change in oxidation-number from +6 (the sum of the numbers for 2 atoms of C) to +8 (for 2 atoms of C), or two units of oxidation per molecule of $H_2C_2O_4$. The manganese undergoes a change in oxidation-number from +7 to +2, or five units of reduction per molecule of $KMnO_4$. Therefore the reagents interact in the ratio of five molecules of $H_2C_2O_4$ to two molecules of $KMnO_4$.

(25) $$Ca(HC_2O_4)_2 + KMnO_4 + HNO_3 = CO_2 + Ca(NO_3)_2 + KNO_3 + Mn(NO_3)_2 + H_2O$$

The carbon undergoes a change in oxidation-number from +12 (the sum of the numbers for 4 atoms of C) to +16 (for 4 atoms of C), or four units of oxidation per molecule of $Ca(HC_2O_4)_2$. The manganese undergoes a change in oxidation-number from +7 to +2, or five units of reduction per molecule of $KMnO_4$. Therefore the reagents interact in the ratio of five molecules of $Ca(HC_2O_4)_2$ to four molecules of $KMnO_4$.

(26) $$K_2Fe(C_2O_4)_2 + KMnO_4 + HNO_3 = CO_2 + Fe(NO_3)_3 + KNO_3 + Mn(NO_3)_2 + H_2O$$

The iron undergoes a change in oxidation-number from +2 to +3, and the carbon undergoes a change in oxidation-number from +12 (the sum of the numbers for 4 atoms of C) to +16 (for 4 atoms of C), or 5 units of oxidation (for 1 atom of Fe and 4 atoms of C) per molecule of $K_2Fe(C_2O_4)_2$. The manganese undergoes a change in oxidation-number from +7 to +2, or 5 units of reduction per molecule of $KMnO_4$. Therefore the reagents interact in the ratio of one molecule of $K_2Fe(C_2O_4)_2$ to one molecule of $KMnO_4$.

(27) $$NH_4Cl + NH_4NO_3 = Cl_2 + N_2 + H_2O$$

The nitrogen (of NH_4Cl) undergoes a change in oxidation-number from -3 to 0, and the chlorine undergoes a change in oxidation-number from -1 to 0, or a total of four units of oxidation per molecule of NH_4Cl. The nitrogen (of NH_4NO_3) undergoes a change in oxidation-number from $+2$ for 2 atoms (i.e., -3 for the first atom and $+5$ for the second atom) to 0, or two units of reduction per molecule of NH_4NO_3. Therefore the reagents interact in the ratio of one molecule of NH_4Cl to two molecules of NH_4NO_3. (To supply an even number of atoms of Cl and N for the products, these numbers are doubled.)

(28) $$Zn + HNO_3 = Zn(NO_3)_2 + NH_4NO_3 + H_2O$$

The zinc undergoes a change in oxidation-number from 0 to $+2$, or two units of oxidation per atom of Zn. The nitrogen undergoes a change in oxidation-number from $+5$ to -3 (in NH_4 radical of NH_4NO_3), or eight units of reduction per molecule of HNO_3. Therefore the reagents interact in the ratio of four atoms of Zn to one molecule of HNO_3, so far as oxidation-reduction is concerned. But nine more molecules of HNO_3 are needed to supply nitrate radical for the $Zn(NO_3)_2$ and NH_4NO_3, or ten molecules of HNO_3 altogether.

§329. Reduction Potentials

Before leaving the subject of oxidation-reduction reactions, it should be emphasized again that the writing of a balanced equation tells little of the readiness with which the reaction will take place or the influence of various conditions on the reaction. Thus, oxidants and reductants vary enormously in strength, but there is no necessary connection between the strength of an oxidant and the rate at which it will carry out a particular oxidation. Hydrogen peroxide is a stronger oxidant than free iodine, as shown by the fact that it readily oxidizes HI to I_2. But iodine will oxidize a thiosulfate (to tetrathionate) more rapidly than will hydrogen peroxide, as shown by the fact that an iodine solution is instantly decolorized by a thiosulfate solution, while the addition of excess of hydrogen peroxide to a solution containing both KI and $Na_2S_2O_3$ (slightly acid), results in the production of the brown color of free iodine only after an appreciable time interval (which may easily be varied by proper attention to conditions and concentrations all the way from a few seconds up to several minutes, just as in the case of other "clock reactions"). An illustration of the effect of conditions on the readiness with which reactions occur, is found in the reaction of metallic silver with hydrogen sulfide. According to the relative positions of hydrogen and silver in the electromotive series, one would conclude that silver would not react with acids to displace hydrogen. This conclusion is confirmed by the fact that metallic silver is not attacked

by dilute sulfuric acid. But metallic silver is acted upon fairly readily by hydrogen sulfide, with formation of silver sulfide and hydrogen. The disturbing fact here that makes the first guess wrong is the extreme insolubility of silver sulfide. Another striking case may be mentioned. Potassium permanganate is one of the strong oxidants, readily oxidizing hydrochloric acid to chlorine. Since hydrobromic acid is a stronger reductant than hydrochloric acid, potassium permanganate should oxidize hydrobromic acid still more readily than it does hydrochloric acid. Experimental trial confirms this conclusion. But if a solution of manganous ion, containing a little cupric ion, is treated with an excess of sodium hydroxide and chlorine (or even bromine), the manganese will be oxidized to a manganate and finally to permanganate. Thus, the difference in conditions of having the solution acid or alkaline (plus Cu^{++} as catalyst), makes all the difference between permanganate ion oxidizing bromide ion to bromine, with reduction of the permanganate to manganous ion; and bromine oxidizing manganous ion to permanganate ion, with reduction of the bromine to bromide ion.

To a large extent, these differences in strength of oxidants and reductants, rates of reaction, and effect of conditions, are specific bits of information concerning individual reagents and particular reactions. For ionic reactions in aqueous solutions, a great deal has been done toward organizing parts of this information by arranging the lists of oxidants and reductants in a series (of which the electromotive series of the metals is a part), with specific electric potentials to indicate the position, under " standard conditions," of each reagent in the series.

A consideration of facts developed in connection with the ion-electron method of balancing ionic equations, serves as a useful introduction to this subject. Thus in the partial equations used to represent the reduction and the oxidation separately, it becomes evident that the oxidant uses up electrons and the reductant supplies electrons. On that basis, if the oxidants and reductants were placed in separate beakers, the two solutions connected by a " salt-bridge " (an inverted U-tube filled with a salt solution, and arranged to prevent syphoning of the solution from one beaker to the other), and then the circuit completed by running a wire from one solution to the other, electrons would escape from the beaker containing the reductant and enter the one containing the oxidant, thus permitting the reaction to take place. Thus the oxidant would be reduced and the reductant oxidized, without the reagents coming in contact with each other. The total amount of current that would flow through the circuit would depend upon the amounts of the reagents present, but the electromotive force set up would depend on the relative strength of the two reagents. Thus for a particular reductant, a strong oxidant would establish a higher E.M.F. than a mild oxidant. By adopting some reductant as standard and measuring the E.M.F. set up (or by measuring the counter E.M.F.

necessary to prevent a flow of electricity), a series of potentials can be obtained for the various oxidants that will express their relative strength as oxidants. The standard reductant with which the oxidants are compared (or to whose value other experimental data are referred by calculation), is the hydrogen electrode, an instrument that was described briefly in an earlier section (p. 118). It will be recalled that this instrument consists of a piece of platinized platinum, saturated with hydrogen, and dipping into a molar solution of HCl. The standard reductant, therefore, is hydrogen, absorbed on the surface of the platinum under atmospheric pressure, in contact with *M* H^+, and at an arbitrarily selected temperature (20° and 25° are the ones most commonly used, with preference shown for the latter in this country). In actual experiments, strong oxidants are positive (electrically) as compared with the hydrogen electrode. As milder oxidants are tested, they become less and less positive, the series passing through zero and becoming negative. This situation of an oxidant becoming negative to a reductant is sufficiently curious to demand some attention. On the basis of the above discussion it can mean only one thing, namely that the hydrogen electrode has changed from being a reductant into an oxidant, and the oxidant being tested is now actually a reductant. This situation becomes understandable so far as the hydrogen electrode is concerned if it be remembered that this consists of hydrogen in contact with hydrogen ion. As a reductant, the hydrogen is converted to hydrogen ion. But hydrogen ion is itself a mild oxidant, reacting with metallic zinc, for instance, to oxidize it to zinc ion ($2\ H^+ + Zn = Zn^{++} + H_2$). Therefore, the hydrogen electrode is not only a standard reductant, but also a standard oxidant. Further, oxidants, acting as such, are reduced to products which can in general, under proper conditions, be reoxidized to the original reagent. Therefore the solution of an oxidant, partly reduced, contains both an oxidant and a reductant. It is to be expected that when a strong oxidant is reduced, the reductant thus formed will be relatively weak. As the strength of the oxidant decreases, the product formed becomes a stronger reductant. Thus it is not surprising, when the matter is considered in greater detail, that the hydrogen electrode is positive toward the weaker oxidants, since such reagents will regularly be accompanied by relatively strong reductants.

The potential of an oxidant depends in part on the concentration of the product to which it is being reduced. Therefore to set up standard values, it is necessary to define the concentration of these materials. When the reagent and the product are both soluble, the concentrations of both should be made *M*; if either is relatively insoluble, the solution should be saturated with respect to that substance and *M* with respect to the other. Thus, the potential assigned a free metal in the oxidation-reduction series is that of the free metal in contact with a molar solution of its positive ion. It is to be noted, in this connection, that one cannot introduce ions into a solution

without adding, at the same time, an equivalent amount of other ions of opposite charge. Thus, to add zinc ion to a solution, it is actually necessary to use some soluble, highly dissociated salt, such as zinc chloride, nitrate, sulfate, or acetate. Also, in the case of salts of the heavy metals (which hydrolyze more or less readily with precipitation of basic salts), it may be necessary to add an appreciable amount of free acid. The assumption is frequently made that these accessory materials are without effect, but it requires only a little thought to realize that these materials themselves may undergo oxidation or reduction, that they may combine with the ions added to form intermediate or complex ions, or that they may serve in other ways to enhance or decrease the activity of the oxidant or reductant. Therefore, the ordinary oxidation-reduction series, with its potential ranging from $+2.9$ to represent the readiness with which lithium is oxidized to lithium ion, down to -1.9, to represent the difficulty with which fluoride ion is oxidized to fluorine, covers a fund of information about the strength of oxidants and reductants under certain specific conditions. These data show with considerable accuracy what may be expected of these reagents in ordinary situations. But they need to be supplemented with a careful statement of the specific conditions under which they apply and the quantitative effect of varying each of these conditions, before they will serve as a complete statement of the oxidation-reduction possibilities of these systems under such a variety of situations as may be used experimentally. A vast amount of attention has been devoted to this subject, both experimentally and theoretically, but it is still far from exhausted. The chief quantitative rules suggested, thus far, are two in number, both based on the application of the law of mass action to the system. The first states that, other things being equal, if the half-reaction is written, every tenfold change in the ratio of concentration of reductant to that of the product to which it is oxidized produces a change in potential of the system equal to $\frac{0.059}{n}$ volts, in which n is the number of electrons formed as product in the balanced half-reaction. The second states that if accessory reagents are used (or products formed) in the half-reaction, the law of mass action should indicate the effect of change of concentration of these materials on the readiness with which the reaction takes place. It is recognized, however, that many reactions take place through a series of intermediate steps, and not infrequently one of these intermediate reactions appears to control the process as a whole.

It need hardly be added that this is a topic worthy of extended treatment in a later course.

TABLE 45

REDUCTION POTENTIALS

Reagent	Potential	Reaction
K..........	+2.924	$K(s)^* = K^+ + \ominus$
Ca..........	+2.76	$Ca(s) = Ca^{++} + 2\ominus$
Mg..........	+1.55	$Mg(s) = Mg^{++} + 2\ominus$
Zn..........	+1.25	$Zn(s) + 2\,OH^- = ZnO(s) + H_2O + 2\ominus$
Mn..........	+1.0	$Mn(s) = Mn^{++} + 2\ominus$
Cu..........	+0.89	$Cu(s) + SH^- + OH^- = CuS(s) + H_2O + 2\ominus$
H..........	+0.83	$H_2(g) + 2\,OH^- = 2\,H_2O + 2\ominus$
Hg..........	+0.77	$Hg(s) + SH^- + OH^- = HgS(s) + H_2O + 2\ominus$
Zn..........	+0.76	$Zn(s) = Zn^{++} + 2\ominus$
Ag..........	+0.67	$2\,Ag(s) + SH^- + OH^- = Ag_2S(s) + H_2O + 2\ominus$
Pb..........	+0.578	$Pb(s) + 2\,OH^- = PbO(\text{s red}) + H_2O + 2\ominus$
Pb..........	+0.575	$Pb(s) + 2\,OH^- = PbO(\text{s yellow}) + H_2O + 2\ominus$
Cr..........	+0.56	$Cr(s) = Cr^{++} + 2\ominus$
S^{--}..........	+0.55	$S^{--} = S(s) + 2\ominus$
Ag..........	+0.51	$Ag(s) + 2\,CN^- = Ag(CN)_2^- + \ominus$
Fe..........	+0.44	$Fe(s) = Fe^{++} + 2\ominus$
Cr..........	+0.4	$Cr^{++} = Cr^{+3} + \ominus$
Cd..........	+0.4	$Cd(s) = Cd^{++} + 2\ominus$
Cu..........	+0.34	$2\,Cu(s) + 2\,OH^- = Cu_2O(s) + H_2O + 2\ominus$
Pb..........	+0.34	$Pb(s) + SO_4^{--} = PbSO_4 + 2\ominus$
Tl..........	+0.33	$Tl(s) = Tl^+ + \ominus$
Pb..........	+0.31	$Pb(s) + 2\,I^- = PbI_2 + 2\ominus$
Co..........	+0.29	$Co(s) = Co^{++} + 2\ominus$
Cu..........	+0.26	$Cu(s) + H_2S(g) = CuS + 2\,H^+ + 2\ominus$
Pb..........	+0.26	$Pb(s) + 2\,Cl^- = PbCl_2 + 2\ominus$
Ni..........	+0.23	$Ni(s) = Ni^{++} + 2\ominus$
VSO_4..........	+0.2	$2\,VSO_4 + 2\,H_2O(l) = (VO)_2SO_4 + 4H^+ + SO_4^{--} + 2\ominus$
Ag..........	+0.15	$Ag(s) + I^- = AgI(s) + \ominus$
Sn..........	+0.13	$Sn(s) = Sn^{++} + 2\ominus$
Pb..........	+0.12	$Pb(s) = Pb^{++} + 2\ominus$
Fe..........	+0.04	$Fe(s) = Fe^{+3} + 3\ominus$
Ag..........	+0.04	$2\,Ag(s) + H_2S(g) = Ag_2S + 2\,H^+ + 2\ominus$
H..........	±0.00	$H_2 = 2\,H^+ + 2\ominus$
Ti^{+3}..........	−0.04	$Ti^{+3} + 2\,SO_4^{--} = Ti(SO_4)_2 + \ominus$
Pb..........	−0.07	$Pb(s) + H_2S(g) = PbS(s) + 2\,H^+ + 2\ominus$
Ag..........	−0.07	$Ag(s) + Br^- = AgBr + \ominus$
Sb..........	−0.1	$Sb(s) = Sb^{+3} + 3\ominus$
Sn^{++}..........	−0.13	$Sn^{++} = Sn^{+4} + 2\ominus$
Cu..........	−0.13	$Cu(s) + Cl^- = CuCl(s) + \ominus$
Sb..........	−0.144	$2\,Sb(s) + 3\,H_2O(l) = Sb_2O_3(s) + 6\,H^+ + 6\ominus$
Bi..........	−0.15	$Bi(s) + Cl^- + H_2O = BiOCl + 2\,H^+ + 3\ominus$
Cu^+..........	−0.17	$Cu^+ = Cu^{++} + \ominus$
Bi..........	−0.2	$Bi(s) = Bi^{+3} + 3\ominus$
Sb..........	−0.21	$Sb(s) + H_2O = SbO^+ + 2\,H^+ + 3\ominus$
Ag..........	−0.22	$Ag(s) + Cl^- = AgCl + \ominus$
As..........	−0.23	$2\,As(s) + 3\,H_2O = As_2O_3(s) + 6\,H^+ + 6\ominus$
Hg_2Cl_2..........	−0.24	$Hg_2Cl_2(s) + 2\,Cl^- = 2\,HgCl_2 + 2\ominus$
PbO..........	−0.27	$PbO(s) + 2\,OH^- = PbO_2 + H_2O + 2\ominus$
Hg..........	−0.275	$2\,Hg + 2\,Cl^- = Hg_2Cl_2 + 2\ominus$
Hg..........	−0.280†	$2\,Hg + 2\,Cl^- = Hg_2Cl_2(s) + 2\ominus$
As..........	−0.3	$As(s) = As^{+3} + 3\ominus$

* s = solid, l = liquid, g = gas.

† Normal calomel electrode ($Cl^- = N$).

TABLE 45 — *Continued*

Reagent	Potential	Reaction
Hg.........	−0.333*	$2\,Hg + 2\,Cl^- = Hg_2Cl_2(s) + 2\ominus$
Cu.........	−0.34	$Cu(s) = Cu^{++} + 2\ominus$
Ag.........	−0.38	$Ag(s) + 2\,NH_3 = Ag(NH_3)_2^+ + \ominus$
OH^-.......	−0.41	$4\,OH^- = O_2(g) + 2\,H_2O + 4\ominus$
$CuCl_2^-$.....	−0.45	$CuCl_2^- = Cu^{++} + 2\,Cl^- + \ominus$
$K_4Fe(CN)_6$	−0.489	$K_4Fe(CN)_6 = K_3Fe(CN)_6 + K^+ + \ominus$
Ag.........	−0.50	$2\,Ag(s) + CO_3^{--} = Ag_2CO_3(s) + 2\ominus$
H_3AsO_3.....	−0.50	$H_3AsO_3 + H_2O = H_3AsO_4 + 2\,H^+ + 2\ominus$
Cu.........	−0.52	$Cu(s) = Cu^+ + \ominus$
I^-.........	−0.53	$2\,I^- = I_2 + 2\ominus$
MnO_4^{--}....	−0.66	$MnO_4^{--} = MnO_4^- + \ominus$
Fe^{++}.......	−0.75	$Fe^{++} = Fe^{+3} + \ominus$
H_2O_2.......	−0.80	$H_2O_2 = O_2(g) + 2\,H^+ + 2\ominus$
Hg.........	−0.80	$2\,Hg(s) = Hg_2^{++} + 2\ominus$
Ag.........	−0.80	$Ag(s) = Ag^+ + \ominus$
Pd.........	−0.82	$Pd(s) = Pd^{++} + 2\ominus$
OH^-.......	−0.84	$2\,OH^- = H_2O_2 + 2\ominus$
Hg.........	−0.86	$Hg(s) = Hg^{++} + 2\ominus$
Hg_2^{++}......	−0.90	$Hg_2^{++} = 2\,Hg^{++} + 2\ominus$
$VOSO_4$.....	−0.92	$VOSO_4 + 2\,H_2O = HVO_3 + SO_4^{--} + 3H^+ + \ominus$
NO.........	−0.95	$NO + 2\,H_2O = NO_3^- + 4\,H^+ + 3\ominus$
Br^-........	−1.06	$2\,Br^- = Br_2 + 2\ominus$
I_2.........	−1.20	$I_2(s) + 6\,H_2O = 2\,IO_3^- + 12\,H^+ + 10\ominus$
Au.........	−1.3	$Au(s) = Au^{+3} + 3\ominus$
Cr^{+3}.......	−1.3	$Cr^{+3} + 4\,H_2O = HCrO_4^- + 7\,H^+ + 3\ominus$
Mn^{++}.......	−1.33	$Mn^{++} + 2\,H_2O = MnO_2(s) + 4\,H^+ + 2\ominus$
Cl^-........	−1.36	$2\,Cl^- = Cl_2(g) + 2\ominus$
Cl^-........	−1.44	$Cl^- + 3\,H_2O = ClO_3^- + 6\,H^+ + 6\ominus$
Au.........	−1.5	$Au = Au^+ + \ominus$
Ce^{+3}.......	−1.5	$Ce^{+3} = Ce^{+4} + \ominus$
Mn^{++}.......	−1.52	$Mn^{++} + 4\,H_2O = MnO_4^- + 8\,H^+ + 5\ominus$
MnO_2.......	−1.63	$MnO_2(s) + 2\,H_2O = MnO_4^- + 4\,H^+ + 3\ominus$
H_2O........	−1.66	$2\,H_2O = H_2O_2 + 2\,H^+ + 2\ominus$
$PbSO_4$......	−1.68	$PbSO_4(s) + 2\,H_2O(l) = PbO_2(s) + 4\,H^+ + SO_4^{--} + 2\ominus$
Co^{++}.......	−1.8	$Co^{++} = Co^{+3} + \ominus$
O_2.........	−1.9	$O_2(g) + H_2O = O_3 + 2\,H^+ + 2\ominus$
F^-.........	−1.9	$2\,F^- = F_2 + 2\ominus$

* Decinormal calomel electrode ($Cl^- = 0.1\,N$).

1. Because of the intimate relation of oxidation and reduction to each other, a reduction series is just the reverse of an oxidation series. In the reduction series, the strong reductants are put at the top of the list, and the weak reductants at the bottom, the order indicating the relative strength of the reagents (in systems in equilibrim, so far as possible, and under standard conditions). If the equations for the reactions were written in the reverse order ($K^+ + \ominus = K(s)$, $Fe^{+3} + \ominus = Fe^{++}$, etc.), the sign of the potential would be reversed, and the list would become an oxidation series, with the weak oxidants at the top and the strong oxidants at the bottom.

2. There is much confusion in the literature concerning the sign to be used with respect to the potentials. The measurement actually made is the E.M.F. of a system, and from this the potential of one of the electrodes is calculated by assuming a definite value for the other as a reference electrode. The basis of the values assigned is the potential of the hydrogen electrode, which is arbitrarily called zero. Since the electropositive character of a metal represents the readiness with which an atom loses an electron and becomes positively charged, the plus sign has been attached to the potentials of those

systems in which the reductant loses electrons more readily than does the hydrogen in the hydrogen electrode, and the minus sign has been attached to the potentials of those systems in which the reductant loses electrons less readily than does the hydrogen in the hydrogen electrode. The opposite convention is frequently adopted; therefore it is necessary to know the approximate character of the system being studied in order to avoid error in the use of data found in the literature.

3. The potential E of an electrochemical reaction is given by the equation:

$$E = E_0 - \frac{0.059}{N} \log_{10} \frac{(A_P)^x}{(A_R)^y}$$

E_0 = potential under standard conditions.
N = Number of electrons in the equation for the reaction.
A_P = activities of the products.
A_R = activities of the reactants.
x and y are the corresponding coefficients in the electrochemical equation.

4. The effect of change in the ratio of concentrations of products to concentrations of reactants is shown in a number of cases in the table. Thus, the reducing power of Hg in contact with M Hg_2^{++}, is represented by a potential of -0.80. By making the solution 0.1 M with respect to Cl^-, and saturated with respect to Hg_2Cl_2, the reducing power of the Hg is raised to -0.333 volts; and by substituting M Cl^- for 0.1 M Cl^-, the potential is raised still higher to -0.280 volts. By lowering the concentration of mercury ion still further through the use of M SH^- and M OH^- (the Hg^{++} precipitating as HgS), the potential is raised to $+0.77$, which indicates a reducing power for Hg of the same order as Zn^0 in contact with M Zn^{++}.

In the same way, if one compares the reducing power of Ag (or the oxidizing power of Ag^+) in solutions containing M Ag^+ ($E = -0.80$), M Cl^- ($E = -0.22$), M I^- ($E = +0.15$), and M CN^- ($E = +0.51$), it becomes evident that there are chemical means available by which the ordinary powers of reagents may be profoundly modified.

5. By proper modification of conditions, it is possible to make reactions effective which might not be thought feasible on the basis of the data in the above table. Thus, in using $CuSO_4$ as a reagent to oxidize I^- to I_2 in the test for I^-, it is assumed that the significant reaction is: $2\ Cu^{++} + 2\ I^- = 2\ Cu^+ + I_2$. According to the table, the potential of the reaction, $Cu^+ = Cu^{++} + \ominus$, is -0.17 volt, while that of the reaction, $2\ I^- = I_2 + 2\ominus$, is -0.53 volt. This would indicate that the reverse reaction might be expected to occur, namely, the oxidation of Cu^+ to Cu^{++} by I_2. But the insolubility of the cuprous salt, or the readiness of formation of a complex anion, together with the marked effect of the acidity of the solution on the reducing power of I^-, make it possible to use this reaction effectively in the qualitative detection of I^-.

6. On the other hand, reactions which might be expected to occur readily, may involve an indirect mechanism such that the data of the table do not apply. The potential of the reaction, $Fe = Fe^{+3} + 3\ominus$ ($+0.04$), would suggest that HCl might oxidize Fe to Fe^{+3}; but the potential of the reaction, $Fe^{++} = Fe^{+3} + \ominus$ (-0.75), indicates that the conversion to Fe^{+3} would be more difficult if the formation of Fe^{++} is an intermediate stage.

Also, the displacement reactions among the metals above hydrogen in the list do not take place readily because of the necessary presence of H_2O and its ions as complicating factors.

7. The data in this table have been taken chiefly from International Critical Tables, Landolt and Börnstein, 4th and 5th editions, and the article by Gerke in *Chemical Reviews*, **1**, 377 (1924–5).

§330. Figure 3. Change in [H+] between N and 0.1 N, corresponding to a change in pH from 0.0 to 1.0.

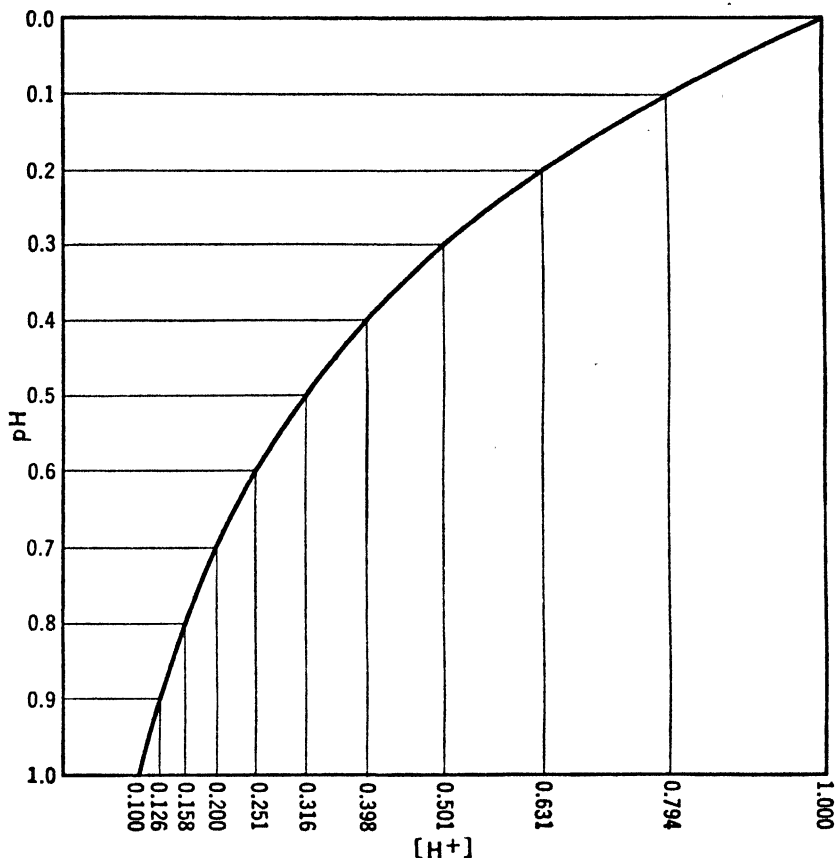



FIG. 3

In the above chart the square is exactly 100 mm. on a side, each tenth of a unit change in the numbers in the vertical line (pH), or horizontal line ([H+]), corresponding to a shift of 10 mm. in position. Thus a pH of 0.1 is represented by a point in the vertical line 10 mm. down from the top. This corresponds to a [H+] of 0.794 N, which is represented by a point on the bottom line 79.4 mm. from the left end. A pH of 0.2 is represented by a point 20 mm. down from the top, and corresponds to a [H+] of 0.631 N, which is represented by a point 63.1 mm. from the left. Values intermediate to these may be determined by finding the point on the curve horizontally opposite the given pH and vertically above the corresponding [H+].

Because of the logarithmic character of *p*H, this same chart may be used to show the change in $[H^+]$ between 0.1 *N* and 0.01 *N*, corresponding to a change in *p*H from 1.0 to 2.0, by merely adding one unit to the values in the vertical column, and dividing the values in the horizontal line by 10 (i.e., moving the decimal point one place to the left). Thus a *p*H of 1.1 corresponds to a $[H^+]$ of 0.0794 *N*, a *p*H of 1.2 corresponds to a $[H^+]$ of 0.0631 *N*, etc. For a *p*H range from 5 to 6, the values for $[H^+]$ will be those in the chart with the decimal point moved five places to the left.

Since the *p*H system of discussing acidity is seldom employed in the higher acidities, there is little occasion to be concerned with the *p*H of a solution in which the $[H^+]$ is greater than unity. For completeness of discussion, however, it may be noted that *p*H values become negative as the values for the $[H^+]$ become greater than one. The chart may be used to show these relations by subtracting one unit from the values for *p*H in the vertical column and multiplying the values in the horizontal column by 10. Thus a *p*H of -0.1 (or 0.9–1.0) corresponds to a $[H^+]$ of 1.26 *N*, a *p*H of -0.5 (or 0.5–1.0) corresponds to a $[H^+]$ of 3.16 *N*, and a *p*H of -1.0 (or 0.0–1.0) corresponds to a $[H^+]$ of 10.0 *N*.

§331. THE PERIODIC SYSTEM OF THE ELEMENTS

0	I	II	III	IV	V	VI	VII	VIII		
R	RH R_2O	RH_2 RO	RH_3 R_2O_3	RH_4 RO_2	RH_3 R_2O_5	RH_2 RO_3	RH R_2O_7	RO_4		
He 2 4.002	Li 3 6.940	Be 4 9.02	B 5 10.82	C 6 12.00	N 7 14.008	O 8 16.0000	F 9 19.00			
Ne 10 20.183	Na 11 22.997	Mg 12 24.32	Al 13 26.97	Si 14 28.06	P 15 31.02	S 16 32.06	Cl 17 35.457			
A 18 39.944	K 19 39.10	Ca 20 40.08	Sc 21 45.10	Ti 22 47.90	V 23 50.95	Cr 24 52.01	Mn 25 54.93	Fe 26 55.84	Co 27 58.94	Ni 28 58.69
	Cu 29 63.57	Zn 30 65.38	Ga 31 69.72	Ge 32 72.60	As 33 74.93	Se 34 79.2	Br 35 79.916			
Kr 36 83.7	Rb 37 85.44	Sr 38 87.63	Y 39 88.92	Zr 40 91.22	Cb 41 93.3	Mo 42 96.0	Ma 43	Ru 44 101.7	Rh 45 102.91	Pd 46 106.7
	Ag 47 107.880	Cd 48 112.41	In 49 114.8	Sn 50 118.70	Sb 51 121.76	Te 52 127.5	I 53 126.92			
Xe 54 131.3	Cs 55 132.81	Ba 56 137.36	* 57–71	Hf 72 178.6	Ta 73 181.4	W 74 184.0	Re 75 186.31	Os 76 190.8	Ir 77 193.1	Pt 78 195.23
	Au 79 197.2	Hg 80 200.61	Tl 81 204.39	Pb 82 207.22	Bi 83 209.00	Po 84	85			
Rn 86 222	87	Ra 88 225.97	Ac 89	Th 90 232.12	91	U 92 238.14				

* Rare Earths:

La	Ce	Pr	Nd	Il	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
138.92	140.13	140.92	144.27	—	150.43	152.0	157.3	159.2	162.46	163.5	167.64	169.4	173.5	175.0

INDEX

INDEX

NOTE. — *Anyone using this book frequently will probably save time by becoming acquainted with the order of details under the individual metals and non-metals.*

Metals. — *The discussion of each metal is divided into ten parts numbered and arranged as follows:*

1. **Physical Properties**
   Density, melting point, boiling point, color, ductility, etc. Uses. Alloys.
2. **Occurrence**
   Ore deposits; amount of metal produced annually; price.
3. **Preparation**
   The more important commercial methods.
4. **Oxides and Hydroxides**
   These are arranged in order of increasing valence.
5. **Solubilities**
   a. Metal. b. Oxides and hydroxides. c. Salts.
6. **Reactions with various reagents**
   a. Hydroxides: $NaOH$, NH_4OH.
   Carbonates: CO_3^{--}, HCO_3^-.
   b. Organic acids and salts: oxalate, acetate, cyanide, ferrocyanide, ferricyanide, thiocyanate.
   c. Nitrite, nitrate, hydrogen peroxide.
   d. Phosphorus acids and salts: hypophosphite, phosphite, phosphate (ortho-, meta-, pyro-).
   e. Sulfur acids and salts: sulfide, thioacetate, thiosulfate, sulfite, sulfate.
   f. Halogen acids and salts: fluoride, chloride, chlorate, bromide, (bromate), iodide, (iodate).
   g. Arsenite, arsenate, stannite.
   h. Chromate, molybdate and some others not closely related to any of the above.
7. **Ignition**
8. **Detection**
   a. With inorganic reagents.
   b. With organic reagents.
9. **Determination**
   a. Gravimetric. b. Volumetric. c. Colorimetric.
10. **Oxidation and Reduction**

Non-metals. — *The non-metals are discussed in the order of increasing atomic weight. The divisions and sequence vary slightly from those under the metals.*

1. **Physical Properties**
2. **Occurrence** *(if important)*
3. **Preparation**
4. **Hydrides, Oxides and Acids**
   When sufficiently important the acids are discussed in separate sections following that on the non-metal itself. The order is that of increasing valence, e.g., Cl_2, HCl, $HClO$, $HClO_2$, $HClO_3$, $HClO_4$.
5. **Solubility**
6. **Reactions**
   a. With metals and their compounds.
   b. With non-metals.
7. **Ignition**
8. **Detection**
9. **Determination**
10. **Oxidation and Reduction**

Summarized Index for the Metals

Summarized Index for the Non-Metals